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A DIVISION OF

AEROJET-GENERAL CORPORATION

APPLICABILITY OF AQUEOUS SOLUTIONS TO THE REMOVAL OF SO_2 FROM FLUE GASES

FINAL REPORT

VOLUME I

PREPARED UNDER CONTRACT PH 86-68-77

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U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
CINCINNATI, OHIO

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The program included: literature survey; preliminary economic evaluation for comparative purposes; selection of candidate processes; laboratory experimentation to demonstrate, simplify and improve candidate processes: and process simplification and improvement of each candidate existing process; demonstration of process feasibility of any candidate new process; plant-scale evaluation and cost estimates for the candidate processes to both new and existing power plant facilities and to a new smelter facility. Of the four candidate processes the Zinc Oxide process was considered to merit further study, both in the form of a fluidized bed and in the form of the original Na+ scrubbing process to the small-scale pilot stage. The three remaining candidate processes (Cominco Exorption, Ammonia-Hydrazine Exorption, and Mitsubishi Lime) are not considered to be as economically attractive as the original Johnstone process. A major problem confronting any aqueous process in which sulfur dioxide is recovered as such is that of oxidation in the scrubber. Nearly 700 references are listed, with an author index.

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VOLUME I

October 1970

by

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Prepared under Contract PH 86-68-77 by the
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PART ONE

GENERAL

I. INTRODUCTION

The initial objective of Contract No. PH 86-68-77 was to assay the feasibility of using aqueous systems for removing sulfur dioxide from flue gases. The period of service of the initial program was from 29 December 1967 to 31 May 1969. This technical effort is reported in Volume I, "Applicability of Aqueous Solutions to the Removal of SO_2 from Flue Gases." An extension of this program covered the period 31 May 1969 to 1 September 1970. This part of the program is reported in Volume II, "The Development of New and/or Improved Aqueous Processes for Removing SO_2 from Flue Gases."

The general discussion, Part One, consisting of the Introduction, and Summary and Conclusions, is identical in both volumes of this report and provides a resume of the entire project.

The following three phases define the program effort of the initial period:

Phase I. Assessment of Aqueous Solution Methods

- Literature survey
- Preliminary economic evaluation for comparative purposes
- Selection of Candidate processes

Phase II. Laboratory Experimentation Relating to Candidate Processes

- Process simplification and improvement of each candidate existing process
- Demonstration of process feasibility of any candidate new process

Phase III. Preliminary Plant-Scale Process Evaluation and Cost Estimates for the Candidate Processes

- Application of processes selected on the basis of Phases I and II to both new and existing power plant facilities
- Application of processes selected on the basis of Phases I and II to a new smelter facility.

Phase I was accomplished during the first five months of 1968 with Phases II and III conducted concurrently during the remainder of the calendar year.

The following parts of Volume I are concerned with the results of the application of the various tasks listed above. Parts Two to Four cover the work conducted under Phases I, II, and III, respectively. Part Five discusses recommendations for future work under the contract extension. Part Six, "Bibliography" is the result of the extensive literature survey which was carried out at the beginning of Phase I. Nearly 700 references are listed, together with an appropriate author index.

The program extension, designated as Phase IV, consisted of the following tasks:

A. Conceive New Aqueous Scrubbing Processes.

B. Develop Improvements to Previously Conceived Aqueous Scrubbing Processes.

C. Determine the Degree to Which Inadvertent Sorbent Oxidation Can Be Minimized.

D. Determine the Degree of Interference Which Inadvertent Sorption of NO_x Has On SO_2 Removal Efficiencies.

E. Support the Laboratory Investigations with Preliminary Process Evaluations and Economic Analyses.

The tasks of Phase IV are covered in Parts Two through Six of Volume II.

II. SUMMARY AND CONCLUSIONS

A. VOLUME I

Approximately 500 technical documents, selected from the bibliography of Part Six, were collected, catalogued, and reviewed for the identification and description of various aqueous processes which have been used, or are currently being investigated, developed, or used for the removal of sulfur dioxide from flue gases. Some thirty processes were identified, and of these sufficient data were available for a preliminary economic evaluation of twenty-two. As a result of the evaluation the following four processes were considered to merit further investigation:

- Zinc Oxide Process (Sodium Sulfite Scrubbing)
- Cominco Exorption Process (Ammonium Sulfite Scrubbing)
- Ammonia-Hydrazine Exorption Process (Hydrazine Scrubbing)
- Mitsubishi Lime Process (Lime water Scrubbing)

The Ammonia-Hydrazine Exorption process, conceived at Aerojet, represented a paper study, subject to an experimental demonstration of process feasibility.

Following process selection, a laboratory program was conducted relating to process demonstration and/or improvement. Attempts to improve the Zinc Oxide process were mainly concerned with lowering the calcination temperature required for the release of sulfur dioxide from the regeneration feed, zinc sulfite. No significant improvements were effected, but the investigation led to the conception of a new process based on the use of zinc oxide, in which a fluidized bed of this material is used directly for the low-temperature (50°C) sorption of sulfur dioxide. The feasibility of the concept was demonstrated in the laboratory.

The Cominco Exorption process suffers from the relatively high steam costs associated with the desorption of sulfur dioxide from aqueous ammonium bisulfite solution. The use of acids as promoters for this reaction was therefore investigated. Although several acids were found to be partially effective it was found that the cost of the acid, the additional complexity to the process caused by the use of the acid, and other factors would not be compensated by the limited reduction in steam requirements which might be attainable in this manner. It was concluded, therefore, that this process must be considered as uneconomical.

The Ammonia-Hydrazine Exorption process was designed to combat the high steam requirements of the Cominco Exorption process through the use of hydrazine as the absorbent for sulfur dioxide. Since hydrazine salts are highly soluble in aqueous media it appeared that the desorption of sulfur dioxide from aqueous hydrazine bisulfite might be effected without the simultaneous volatilization of large quantities of water. As the result of an experimental program designed to demonstrate process feasibility, it was found that concentrated hydrazine sulfite solution readily absorbed sulfur dioxide under simulated process conditions. However, an unavoidable loss of hydrazine by oxidation occurred during the regeneration reaction, so that any savings in steam costs through the use of this method was nullified. Therefore, the process was no longer regarded as economically feasible.

No experimental work was indicated relating to the Mitsubishi Lime process. The process was regarded as economical, provided that by-product gypsum could be sold in quantity. However, a subsequent market survey indicated that gypsum requirements could readily be filled from natural deposits and that no appreciable synthetic gypsum market exists at the present time. A simplified version of the process, in which the gypsum is discarded as waste, appeared more attractive. A laboratory effort was not considered to be needed for the simplified process.

In addition to the laboratory effort described above, which was designed to overcome problems associated with specific processes, some attention was also directed to a problem which is common to all aqueous scrubbing methods in which sulfur dioxide is recovered as such; namely, the oxidation of sulfite to sulfate in the absorber. The literature indicates that in some processes oxidation can amount to 10 to 14% or more (expressed as a percentage of the incoming SO_2). It was planned to investigate the extent to which oxygen and nitrogen oxides in flue gas contribute to oxidation, and to investigate the use of various oxidation inhibitors, such as hydroquinine, for its prevention. Work in this area was initiated toward the end of the contract period, and was completed during the second year of the program (Phase IV). The results are reported in Volume II.

Of the four candidate processes, only the Zinc Oxide process (Na^+ scrubbing/ZnO regenerant) was considered for a complete evaluation in Phase III. Thus, process evaluations and cost estimates were completed for large new and existing power plants, a small existing power plant, and for an existing smelter facility. An evaluation was begun on the simplified lime process, but was not completed since the analysis of limestone systems was being done on another contract.

The major conclusions which were drawn from the work reported in Parts Two to Four of Volume I, are the following:

- Of the four candidate processes which were selected for further study as the result of the Phase I effort, the Zinc Oxide process was considered to merit further study, both in the form of a fluidized bed system, as proposed by Aerojet, and in the form of the original Na^+ scrubbing process, as developed by Johnstone to the small-scale pilot stage. For the Johnstone process available data in Phase III indicated that for a large power plant (2.5 MMSCFM of flue gas) to be operated at break-even conditions, product sulfuric acid would have to be salable at almost \$25/ton (assuming a 70% load factor and an SO_2

feed gas concentration of 3000 ppm). If, however, the product acid from this plant could be sold for only $10/ton, the operation of this "add-on" SO_2 control process would represent a net cost to the utility of about $1.23/ton of coal burned. Applied to a medium-sized smelter effluent (220,000 SCFM of the flue gas), the Johnstone process could be operated at break-even conditions, if product sulfuric acid were sold at about $18/ton.

- The three remaining candidate processes (Cominco Exorption, Ammonia-Hydrazine Exorption, and Mitsubishi Lime) are not considered to be as economically attractive as the original Johnstone process.
- A major problem confronting any aqueous process in which sulfur dioxide is recovered as such is that of oxidation in the scrubber. Such oxidation inevitably leads to the formation of sulfate, which is in general less readily isolated from aqueous solution and less readily decomposed than the corresponding sulfite. As a result it may be anticipated that equipment and operating costs will increase, and product yields will decrease, in proportion to the extent of oxidation encountered.

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B. VOLUME II

In the area relating to new aqueous processes for the removal of SO_2 from flue gas, attention has been focused on the use of fluidized solids as absorbents. The absorption step, which is conducted at 50° to $60^\circ C$, requires the presence of appreciable water in the gas phase, and this is provided largely through the use of an aqueous prescrubber. The prescrubber also serves the function of removing SO_3 and fly ash from the raw gas.

Only basic materials have proved suitable as SO_2 absorbents. It was found, for example, that both alkali (Na, K) and alkaline earth (Mg, Ca) sulfites are too weakly basic to absorb, but that carbonates (Na) and oxides (Zn, Mg) are good absorbers. For example, when zinc oxide was used it was found that more than 50 g of SO_2 was absorbed per 100 g of the oxide before SO_2 removal efficiency dropped below 90%.

A problem that arises in all regenerative aqueous SO_2 scrubbing processes is that a portion of the absorbent becomes oxidized by the O_2, fly ash, and/or NO_x components of flue gas. This is highly undesirable, inasmuch as the absorbent cannot readily be regenerated for reuse from the oxidized product. The extent of oxidation appears to be substantially less for essentially dry fluidized bed absorbents than for bulk water systems, and in particular fly ash, which tends to catalyze the oxidation in bulk water systems, was determined to be without effect when incorporated into a dry fluidized zinc oxide absorber.

Of the three gaseous oxidizing components of flue gas (O_2, NO, and NO_2), it was found that NO_2 is by far the most active, and that fluidized zinc oxide was partially converted to sulfate when both SO_2 and NO_2 were present in the influent gas. It was discovered, however, that oxidation of the bed material could be essentially eliminated through the incorporation of ferrous ion into the aqueous prescrubber. The main function of the ferrous ion is considered to be that of reducing NO_2 to NO. For an influent gas containing all flue gas components, less than one-half percent of the SO_2 absorbed by zinc oxide was converted to sulfate when the prescrubber contained 1% ferrous sulfate. In the practical case, ferrous ion would be provided to the prescrubber in the form of scrap iron.

It may be presumed that the use of fluidized solids as SO_2 absorbents will be attended to some extent by the attrition of solid particles, and consequently some attention was devoted to a study of both particle size and particle activity when zinc oxide was used as the absorbent. It was found that commercially available, large pelleted oxide particles are readily attrited to fine particles, but that if the oxide is first converted to the sulfite through SO_2 absorption, and the sulfite is then thermally decomposed, the resulting regenerated oxide shows considerable resistance to attrition. Recent studies have indicated that both zinc sulfite and regenerated zinc oxide in the range of -12 to +24 mesh can be utilized with considerable resistance to attrition at a superficial gas velocity of about 3 feet per second. It was also found that the regenerated oxide is much more active toward SO_2 absorption than is the fresh, unused commercially available oxide.

In the area relating to process improvement, attention was directed toward the thermal decomposition of metallic sulfites, inasmuch as these compounds are the principal products resulting from the absorption of SO_2 by metallic oxides and hydroxides, and because the regeneration of the oxides from the sulfites is probably best accomplished by thermal means. The decomposition reaction is always attended to some extent by the formation of sulfate, and other products, as a result of the disproportionation of the sulfite.

The thermal decomposition of zinc sulfite was studied in both muffle and tube furnaces as a function of time and temperature. An important result of this work was the discovery that the rate of the decomposition reaction was markedly increased in the presence of steam. It was subsequently found that the use of steam permitted the decomposition to be carried out at temperatures ($<300^\circ C$) below which disproportionation occurs, so that the formation of sulfate and sulfide could be essentially avoided. In another series of experiments it was found that the use of steam was much less effective in promoting the decomposition of zinc sulfate.

The disproportionation of magnesium sulfite is more extensive than that of zinc sulfite, and it might be expected that the use of steam would be less effective in the case of magnesium. Preliminary experiments have shown that the temperatures required for the decomposition of magnesium sulfite are substantially decreased through the use of steam, but that the formation of appreciable sulfate attends the decomposition.

As a result of the experimental work considered above relating to the use of fluidized zinc oxide as an absorbent for SO_2, a tentative system was formulated involving the recovery of the SO_2 as such. The overall system involves the use of an aqueous prescrubber, the removal of SO_2 from the water-saturated gas by the oxide, and the thermal decomposition of the resulting sulfite at 275°C for the regeneration of the oxide and the recovery of SO_2. Any zinc sulfate formed is separately decomposed at higher temperatures, and no waste product results. In an alternative system, sulfate is removed by filtration rather than by calcination. To accomplish this, a portion of the sulfite-sulfate mixture is dissolved in aqueous SO_2 and the sulfite is reprecipitated with zinc oxide. After filtering the zinc sulfate solution, the sulfite cake is returned to the process.

The studies on oxidation and oxides of nitrogen in aqueous solution scrubbing systems were combined due to the contributions of nitrogen oxides to sorbent oxidation. Most of the experiments were made with sodium sulfite-bisulfite solutions similar to that used in the Johnstone Zinc Oxide process. A "once through" countercurrent absorption column was used in most of these tests. Fresh absorbent solution was fed to the top of the column and the spent solution removed from the bottom. Another arrangement was used for some tests in which the absorbent was recirculated through the column. Other absorbent systems checked were potassium sulfite-bisulfite, and magnesium, calcium, and sodium hydroxide solutions.

Commercially available inhibiting and complexing agents, widely used in other applications, were screened for their ability to reduce oxidation of sulfur dioxide (sorbent) in the scrubber. Oxidation of the sorbent due to oxygen or fly ash in the flue gas was suppressed by some of the materials. When nitrogen oxides were present in the flue gas, however, oxidation was lowered only by using nitrilotriacetic acid, and this inhibitor was effective only in a potassium sulfite-bisulfite solution having a pH of 12.6.

It was found that, although oxygen in the flue gas contributes to the oxidation of the sorbent during scrubbing, the high levels of oxidation was progressively greater as the concentration of nitrogen dioxide in the flue gas was increased. The rate of oxidation was highest in tests made with 400 ppm each of nitrogen oxide and nitrogen dioxide.

Fly ash did not significantly increase oxidation in systems where fly ash free absorbents were fed to the once through column. In absorbent recirculating systems, in which the fly ash accumulated and some of the iron content was solubilized, a low level of SO_2 oxidation was experienced. The oxidation increased with increasing turbulence in the system. A similar effect was found when ferric ions such as $Fe_2(SO_4)_3$ were added to the system.

Saturating the sodium sulfite-bisulfite scrubbing solution with sodium sulfate inhibits oxidation. This is explained by the limited solubility of oxygen in high ionic strength aqueous solutions.

Since oxygen is only slightly soluble in water, the liquid phase is the limiting resistance to the absorption of the oxygen. Thus, increasing turbulence in the scrubber improves the absorption of oxygen and the amount of oxidation of the sorbent increases with the turbulence of the system.

As discussed in Part Three, a prescrubber circulating a solution containing ferrous ion removes the nitrogen dioxide from the flue gas stream. Using this prescrubber system in conjunction with aqueous solution scrubbers also reduced oxidation of the sorbent to a very low level due to removal of the nitrogen dioxide.

Although additional investigations would be needed to verify the data, it seems that the absorption of nitrogen oxides simultaneously with sulfur dioxide is about the same quantity as the percent nitrogen dioxide in the flue gas. The experiments also indicate that the absorption of NO_x into SO_2 scrubbing solutions has no effect on SO_2 removal efficiency.

Miscellaneous process and economic evaluations were made on the Johnstone Zinc Oxide process, the new Fluidized Zinc Oxide process, and a Magnesium Base Slurry SO_2 Scrubbing system.

Evaluations involving the Johnstone Zinc Oxide process included an analysis in which sulfur dioxide recovered from the absorbent was converted to sulfur using the Asarco process. If product sulfur could be sold for $20 per long ton, the net cost of operating this SO_2 removal/sulfur recovery process on a 1400 MW power plant (at a 70% load factor) would approximate $1.36 per ton of coal burned. The economics of converting the sulfur dioxide to sulfuric acid (see Volume I) was re-evaluated on the basis of lower sales prices for the sulfuric acid produced. An analysis of using reverse osmosis to separate the oxidation product from the absorbent indicated an uneconomical system based on current technology.

The evaluation of the optimized new Fluidized Zinc Oxide process showed relatively low capital and operating costs for a system serving a 1400 MW power plant; however, it must be recognized that this projection is based on the presumed validity of data that has been generated on a very small-scale laboratory equipment.

The cost study of the Magnesia Base Slurry SO_2 Scrubbing system was made only on the absorption system. An evaluation of the regeneration system, which was not available, would have to be made to complete the analysis.

The major conclusions which have been drawn from the work reported in Parts Two to Six of Volume II are the following:

- Efficient absorption of SO_2 at flue gas concentrations can be effected through the use of dry, fluidized basic materials in the range of 50° to 60°C, if sufficient water is incorporated into the gas phase upstream of sorbent contactor.

- The formation of sulfate can be essentially eliminated in a fluidized bed absorber, and reduced to a very low value in an aqueous absorber, through the use of ferrous ion in an aqueous prescrubber to reduce NO_2 to NO.
- The thermal decomposition of both zinc and magnesium sulfites is markedly promoted by the presence of steam. The use of steam permits the decomposition of zinc sulfite to be carried out at a temperature below that at which disproportionation occurs.
- A new process for the removal of SO_2 from flue gas is described in which dry fluidized zinc oxide is used as the absorbent. The oxide is recovered for reuse upon thermal decomposition of the resulting sulfite, and the liberated SO_2 is recovered as such. Little or no sulfate is formed.
- NO_x (especially NO_2) is the major contributor to oxidation of the sorbent in aqueous solution systems.
- In general, the inhibitors and complexing agents investigated did not lower the level of oxidation in the presence of NO_x in the flue gas.
- The level of oxidation is less in sorbent solutions saturated with an inert salt.
- The efficiency of SO_2 removal from flue gas is not affected by the presence of NO_x.
- The economics of the conceptualized fluidized-bed zinc oxide process appear to be superior to other regenerable processes for the removal of SO_2 from flue gases, but the state of development of this process is in its very early stage.

One, merely tentative, "conclusion" bears mentioning:

- It appears that adding NO_2 to flue gas to obtain an equimolar ratio of NO/NO_2 prior to scrubbing the gas with aqueous sulfite-bisulfite solutions or slurries, for SO_2/NO_x removal will not lower the NO_x content of the gas significantly, but will cause unwanted oxidation of the sulfite to sulfate to increase drastically.

PART TWO

ASSESSMENT OF AQUEOUS SOLUTION METHODS - PHASE I

I. INTRODUCTION

A comprehensive literature survey constituted the first task required in Phase I. The information generated from the survey provided the basis for assessment of the many aqueous-based scrubbing processes which have been developed over a period dating back to the latter part of the 19th Century. Typical information related to process development application, process reactions, equipment, by-product recovery, economics, etc.

The assessment was based on a comparative economic evaluation of the various processes. Some of the factors considered in the study were capital and operating costs, by-product utilization and/or disposal including related credits or debits, and a pragmatic consideration of the effect or impact of high-volume production of by-products upon future markets.

As the result of the Phase I effort several candidate processes were selected for further consideration in Phases II and III. However, the work beyond Phase I was not considered to be limited to the chosen processes; if one or more promising aqueous scrubbing methods were conceived during the later stages of the program, they would also be analyzed in due course.

It is emphasized that the results reported herein are based on a comparative economic analysis of aqueous scrubbing systems. As such, one can interpret the results on a relative basis for the systems considered. However, a comparison of any of the costs cited for a specific process (e.g., operating cost per ton of coal consumed) with analogous costs derived from the work of other investigators should be done with extreme caution. This is particularly true if a non-aqueous process is being compared with one or more of the aqueous processes reported here. One can make such comparisons only after confirmation that the same initial cost considerations are used. The present study is a conservative one in the sense that the process costs are probably high.

II. SUMMARY

A preliminary assessment of aqueous solution methods used for the removal of sulfur dioxide from waste gases was conducted. Of the more than twenty processes that were evaluated on an economic basis, only four were considered as candidates for continued study under Phases II and III. These are the (1) Zinc Oxide, (2) Ammonia-Hydrazine Exorption, (3) Cominco Exorption, and (4) Mitsubishi Lime processes. The Zinc Oxide and Ammonia-Hydrazine Exorption processes both have relatively low capital investment and operating costs; both also generate sulfur dioxide as the main product. The Ammonia-Hydrazine Exorption process can also provide anhydrous hydrazine to the extent that it can be sold, with the unmarketable portion reusable in the process. The Cominco Exorption process is similar to the Ammonia-Hydrazine Exorption process, in that sulfur dioxide is recovered as such. Its capital and operating costs are somewhat higher than those for the other three candidate processes. Steam and heat-exchange equipment costs account in large part for the relatively high cost of this process. The Cominco Exorption process is the only one of the ammonia processes in which sulfur dioxide is the principal product. The Mitsubishi Lime process has low capital and operating costs, and produces a high purity gypsum as the major product. It is the only candidate process that employs a slurry as the absorbent, although this is not considered a significant process disadvantage.

Two processes were considered as marginal candidates. These are the Magnesium Oxide and the Manganese Oxide processes. In both, sulfur dioxide is recovered by calcination of the metal sulfite or sulfate. These processes were eliminated primarily because they compare poorly with the Zinc Oxide process, in which a calcination is also involved. In the latter process the calcination is conducted at a relatively low temperature and yields essentially pure sulfur dioxide; whereas, in the Magnesium and Manganese Oxide processes, a mixture of products is produced at elevated temperatures. Both of the latter processes, as they are described in the literature, also exhibit higher costs than the Zinc Oxide Method.

Relatively high investment and operating costs accounted, in large part, for the elimination of the Haenisch-Schroeder, Ozone-Manganese Ion, Basic Aluminum Sulfate, Sulfidine, and Wet Thiogen processes. The Mitsubishi Red Mud process has a low capital cost but a high operating cost; it too was not considered attractive.

A number of ammonia-based processes were eliminated because their attractiveness is dependent upon an unrealistically high credit for ammonium sulfate. These are the Fulham-Simon-Carves, Showa-Denko, Cominco, Ammonia-Hydrazine, Mitsubishi Manganese Oxyhydroxide, Mitsubishi Ammoniacal Liquor, and Magnesium Hydroxide processes.

Several processes were not considered attractive because sulfur is not recovered in any form. These include the Battersea, Howden-I. C. I. (Cyclic Lime), Mitsubishi Red Mud, and Simplified Lime processes. Another negative feature of these methods is that the by-products formed are solid wastes which pose serious disposal or pollution problems.

A number of processes identified during the course of the work were not evaluated as part of the Phase I effort. Some of these are proprietary, and the limited data available are not sufficient to permit a satisfactory analysis. These include the processes under current development by Wisconsin Electric Power/Universal Oil Products, Combustion Engineering, Bechtel, Ionics/Stone and Webster, and Wellman Lord (Beckwell). The Kanagawa process uses water as a scrubbing medium. Very little data were found on the process. For this reason, and since it is similar to other processes using large volumes of water as the scrubbing medium, it was not evaluated. The Guggenheim process was not considered because it is similar to the Cominco Exorption process except for the method of SO_2 recovery which is discussed later in the text.

The results of the extensive literature review, that yielded nearly 700 papers, reports, patents, etc., provided much of the information needed for the evaluation. Typical information included that pertaining to fundamental absorption phenomena, physico-chemical data, process development and application, by-product recovery, absorbent regeneration, materials of construction, process limitations, and economics. Some of the more important references are cited in this part of the report.

Chemical equilibria calculations were conducted to determine the potential of the various aqueous scrubbing processes for absorbing sulfur dioxide from flue gas. The justification for this work was that the results might have served as a means of readily eliminating processes which theoretically could not be used for reducing the sulfur dioxide content of the flue gas from 0.3% to 150 ppm. Process assessment or analysis would then have been conducted only for the remaining, more promising systems. However, it was subsequently shown that any aqueous scrubbing process can theoretically yield an effluent gas which contains 150 ppm of sulfur dioxide. Accordingly, the only feasible approach to process selection was that involving a direct, comparative economic analysis.

III. TECHNICAL DISCUSSION

A. LITERATURE REVIEW

An extensive literature survey was conducted to collect available data related to processes for removing sulfur dioxide from flue gases by aqueous scrubbing methods. This effort has resulted in the acquisition of an extensive amount of information; for example, some 500 technical papers alone have been acquired.

The literature information has been extensively used in carrying out Phase I of the program. Table 1 lists the processes which have been identified. Some pertinent information for most of the individual processes is also included in the table. The majority of the processes listed in the table have been considered in the economic and technical analysis covered under Phase I; this aspect of the program will be discussed in detail in subsequent sections of the report.

The following method of referencing the literature has been used in this report. In the text itself, references are identified in relation to specific pertinent material which is presented; the references are identified in the Bibliography, Part Six. In addition, a separate group of references for

TABLE 1

AQUEOUS SOLUTION SORPTION PROCESSES FOR REMOVING SO_2 FROM WASTE GASES

Process	Absorber Makeup	End Products	Brief Description	Original Utility	Stage of Development and Present Status
1. Fulham-Simon-Carves	NH_3	$(NH_4)_2SO_4$, S	H_2SO_4 added to scrubber effluent sidestream and mixture autoclaved to produce $(NH_4)_2SO_4$ and S.	Flue gas	Studied extensively on pilot-plant scale in England. Not in current use.
2. Showa-Denko Ammoniacal	NH_3	$(NH_4)_2SO_4$	Air passed through scrubber effluent sidestream to oxidize $(NH_4)_2SO_3$ to $(NH_4)_2SO_4$.	Flue gas	A 25-mw test unit in operation since 1966 at an oil-fired process-stream plant in Japan.
3. Cominco	NH_3	$(NH_4)_2SO_4$, SO_2	SO_2 evolved from scrubber effluent sidestream on acidification with H_2SO_4. $(NH_4)_2SO_4$ also produced.	Smelter gas	In use by Cominco at Trail, B.C. Olin-Mathieson has used process in treatment of acid plant tail gases at Pasadena, Texas plant.
4. Cominco Exorption	NH_3	SO_2, $(NH_4)_2SO_4$	SO_2 stripped from scrubber effluent sidestream by heat (steam). $(NH_4)_2SO_3$ solution returned to scrubber.	Smelter gas	Used by Cominco at Trail, B.C. during World War II.
5. Zinc Oxide	Na_2CO_3	SO_2, $CaSO_4$ (impure)	Addition of ZnO to scrubber effluent sidestream yields $ZnSO_3$ and Na_2SO_3 solution. $ZnSO_3$ calcined to give SO_2 and ZnO, the latter being reused. Na_2SO_3 solution recycled.	Flue gas	Pilot plant in U.S. in 1940's. Prototype in Germany at about same time.
6, 7. Howden-I.C.I. (Cyclic Lime)/Mitsubishi Simplified Lime	Suspension of CaO, $Ca(OH)_2$, or $CaCO_3$	$CaSO_3/CaSO_4$ (impure)	Mixture of $CaSO_3/CaSO_4$ sludge separated from sidestream of scrubber effluent for disposal.	Flue gas	First commercial plant established in Wales in 1930's. Second plant built shortly thereafter in London. Process currently under study by Mitsubishi Heavy Industries, Ltd., Japan.

TABLE 1 (Cont'd)

	Process	Absorber Makeup	End Products	Brief Description	Original Utility	Stage of Development and Present Status
8.	Battersea	Thames River water containing CaO or $CaCO_3$	$CaSO_4$ slurry	Scrubber effluent is treated with $MnSO_4$ to promote oxidation of $CaSO_3$ to $CaSO_4$ which is more suitable for river disposal. Liquid portion of stream returned to scrubber.	Flue gas	British have used process in several power plants.
9.	Magnesium Hydroxide	Suspension of $Mg(OH)_2$	$(NH_4)_2SO_4$	Insoluble $MgSO_3$ formed from absorption is oxidized to soluble $MgSO_4$. The latter is reacted with NH_3 to regenerate $Mg(OH)_2$ which is returned to scrubber; $(NH_4)_2SO_4$ also formed in this step.	Flue gas	Process covered by 1952 British patent. No indication that process was piloted.
10.	Magnesium Oxide	Suspension of MgO	SO_2, $MgSO_4$	$Mg(HSO_3)_2$ formed in scrubber is neutralized with MgO to form insoluble $MgSO_3$. The solid is separated and calcined to regenerate the MgO and yield SO_2.	Flue gas	Process used on a pilot plant scale in USSR prior to 1956. No information on current status there. NAPCA is developing this process under separate contracts.
11.	Manganese Oxide	Suspension of MnO_2	SO_2	Soluble $MnSO_4$ and MnS_2O_6 formed in absorption process. Sidestream from scrubber effluent is heated in autoclave to precipitate these salts which are then calcined to form SO_2 and MnO_2. MnO_2 reused.	Flue gas	Pilot-plant studies conducted by TVA. Not in current use.
12.	Haenisch-Schroeder	Water	SO_2, $CaSO_4$ (impure)	Lime added to scrubber effluent to separate sulfate, formed on oxidation, as $CaSO_4$. Liquid fraction is treated to release SO_2.	Flue gas	Process developed on small scale in late 1800's. Not in current use.

TABLE 1 (Cont'd)

Process	Absorber Makeup	End Products	Brief Description	Original Utility	Stage of Development and Present Status
13. Wet Thiogen	Water	S	Scrubber effluent treated with BaS to form S and mixture of insoluble barium salts. Clarified liquor returned to scrubber. Solids fraction heated to distil off sulfur; residue heated further in furnace with carbon to reduce sulfur salts to sulfide which is reused.	Smelter gas	Process abandoned after some pilot-plant operations. This work appears to have been conducted in early 1900's.
14. Ozone-Mn Ion	Water containing O_3 and $MnSO_4$	H_2SO_4 (dilute)	Ozone added to flue gas promotes oxidation of SO_2. $MnSO_4$ serves as catalyst for oxidation.	Flue gas	Laboratory work conducted at TVA laboratories. Not in current use.
15. Sulfidine	1/1 Mixture of xylidine and water	SO_2, Na_2SO_4	Sidestream from scrubber effluent, containing xylidine sulfite, heated to release SO_2. Xylidine regenerated and returned to scrubber.	Smelter gas	Used in Germany prior and during World War II period. Not in current use.
16. Basic Aluminum Sulfate	$Al(OH)SO_4$	SO_2, $CaSO_4$ (impure)	Scrubber effluent, containing $Al(OSO_2H)SO_4$, heated to release SO_2 and regenerate $Al(OH)SO_4$. Some oxidation to sulfate occurs in scrubber; $CaCO_3$ added to precipitate $CaSO_4$ which is separated and discarded.	Smelter gas	First commercial plant at Imatra, Finland, operated from 1936-41. Plant at Manchester, England in operation in 1958.
17. Ammonia-Hydrazine	N_2H_4	$(NH_4)_2SO_4$	Air passed through scrubber effluent sidestream to oxidize $(N_2H_5)_2SO_3$ to $(N_2H_5)_2SO_4$. N_2H_4 produced in process marketed and/or returned to scrubber system as circumstances permit.	(Flue gas)	Paper study

TABLE 1 (Cont'd)

	Process	Absorber Makeup	End Products	Brief Description	Original Utility	Stage of Development and Present Status
18.	Ammonia-Hydrazine Exorption	N_2H_4	SO_2, $(NH_4)_2SO_4$	SO_2 stripped from scrubber effluent sidestream by heat (steam). Resulting $(N_2H_5)_2SO_3$ solution returned to scrubber. N_2H_4 produced in process marketed and/or returned to scrubber system as circumstances permit.	(Flue gas)	Paper study
19.	Mitsubishi Ammoniacal	NH_3	$(NH_4)_2SO_4$	Air passed through scrubber effluent sidestream to oxidize $(NH_4)_2SO_3$ to $(NH_4)_2SO_4$.	Flue gas	Processes under development by Mitsubishi Heavy Industries, Ltd., Japan. Some pilot-plant work conducted.
20.	Mitsubishi Manganese Oxyhydroxide	Suspension of MnOH(O)	$(NH_4)_2SO_4$	$MnSO_4$ formed in absorption process treated with NH_3 and O_2, regenerating the Mn(OH)O and producing $(NH_4)_2SO_4$.	Flue gas	
21.	Mitsubishi Lime	Suspension of CaO or $CaCO_3$	$CaSO_4$ (pure)	$CaSO_3$ in scrubber effluent oxidized to $CaSO_4$. Fly ash removed upstream of SO_2 scrubber.	Flue gas	
22.	Mitsubishi Red Mud	Suspension of residue from extraction of alumina from bauxite.	Mud containing Na_2SO_4	Sodium aluminum silicate present in the red mud reacts with SO_2 to form Na_2SO_4. Scrubber effluent discarded. Only equipment required is scrubber.	Flue gas	

TABLE I (Cont'd)

	Process	Absorber Makeup	End Products	Brief Description	Original Utility	Stage of Development and Present Status
23.	Wiscon Electric Power/Universal Oil Products	Na_2CO_3	Na_2SO_3/Na_2SO_4	Two-stage system employs direct limestone injection into furnace in combination with wet scrubbing utilizing a Na_2CO_3 solution.	Flue gas	Pilot studies of individual systems carried out. Two-stage system under development.
24.	Combustion Engineering	Water	$CaSO_3/CaSO_4$ (impure)	Dolomitic limestone injected into furnace. SO_3 removed by reaction with calcined limestone. SO_2 and fly ash removed in water scrubber.	Flue gas	Process tested at a mid-western utility power plant. C.E. reportedly installing a $1 million installation at Union Electric Co.'s coal-fired electric power plant in St. Louis County, Missouri.
25.	Kanagawa	Sea water, natural underground water, or alkalized water	-	Process reportedly offers an improved method for attaining intimate contact between water and gas stream.	Flue gas	Pilot-plant studies (10,600 cfh) conducted in Japan.
26.	Wellman-Lord (Beckwell)	K_2CO_3	SO_2	Process believed to involve use of aqueous K_2SO_3 as absorber, with pure SO_2 recovered from calcination of isolated $K_2S_2O_5$.	Flue gas	Process under development.
27.	Bechtel	Limestone		-	Flue gas	Process under development.
28.	Ionics/Stone & Webster	NaOH	H_2SO_4(conc.)	Process involves absorption by aqueous NaOH, and subsequent electrolysis to yield Na_2SO_4.	Flue gas	Process under development.

TABLE 1 (Cont'd)

	Process	Absorber Makeup	End Products	Brief Description	Original Utility	Stage of Development and Present Status
29.	Guggenheim	NH_3	S, $CaSO_4$ (impure)	SO_2 stripped from scrubber effluent sidestream by heat (steam). SO_2 reduced to S by heating with coke. Product $(NH_4)_2SO_4$ treated with lime to regenerate NH_3 which is reused; by-product $CaSO_4$ discarded.	Smelter gas	Pilot plant at Garfield, Utah in 1940's (ASARCO). Process not in current use.
30.	Diethylene Triamine (other amines, e.g., triethylene tetramine and tetraethylene pentamine have also received some initial evaluation)	Diethylene Triamine	SO_2	Amines form solid salts with SO_2 which are soluble in water. SO_2 liberated by heat.	Flue gas	Studied on laboratory scale.

each of the methods examined under Phase I is provided in this part of the report (Section III. D.). A concise statement of the contents of each of the references shown in these groups is included. The groups of references are not considered to be complete as far as literature coverage is concerned. The objective was to provide the reader with select information on some of the more important papers, patents, text books, etc.

B. THEORETICAL CHEMICAL EQUILIBRIA CONSIDERATIONS*

1. Conclusions

Chemical equilibria calculations were conducted to determine the potential of the various aqueous scrubbing processes for absorbing SO_2 from flue gas. It was considered that the results of this work might have served as a means of readily eliminating processes which theoretically could not possibly reduce the SO_2 content of the flue gas from 0. 3% (3000 ppm) to 150 ppm. Economic analyses would then have been carried out for the remaining processes.

The results of the study show, however, that essentially all of the known aqueous processes can yield an effluent gas which contains 150 ppm of SO_2. Accordingly, the only feasible approach to eliminating the "poorer" processes appears to be by the direct economic analysis route.

2, Comments on the SO_2-Removal Efficiency of Specific Types of Processes

Most of the aqueous processes utilize a scrubbing medium which is a solution (as contrasted with a suspension). Examples of such processes are the ammonia systems (Fulham-Simon-Carves, Cominco, Showa-Denko, Guggenheim, and Mitsubishi), sodium hydroxide system (Zinc Oxide), water systems (Battersea, Kanagawa, and Haenish-Schroeder), and others. The data shown in Table 2 are representative of the results generated from a series of calculations. Several of these solutions, e. g., the ammonia and sodium hydroxide systems, are of sufficiently high basicity

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*A discussion that covers some of the more theoretical aspects of the calculations, the source of thermodynamic data, etc., is presented as Appendix A in Volume I of this report.

TABLE 2

EQUILIBRIA DATA FOR VARIOUS SCRUBBING SOLUTIONS[*]

Scrubbing Liquor	Major Chemical Constituent	Input Gas (moles)	Input Chemicals (moles)	Stack Loss (moles)	Product (moles)	Capacity (moles/liter H_2O)
1 M NH_3	SO_2	1	-	0.05	0.95	0.17
	H_2O	24.2	69.0	39.1	54.1	-
	NH_3	-	0.97	0.0004	0.97	-
6.5 M NH_3	SO_2	1	-	0.05	0.95	1.5
	H_2O	24.2	19.0	34.1	9.1	-
	NH_3	-	1.2	0.10	1.1	-
6.5 M NaOH	SO_2	1	-	0.05	0.95	1.5
	H_2O	24.2	17.5	32.9	8.8	-
	NaOH	-	1.0	-	1.0	-
H_2O	SO_2	1	-	0.05	0.95	0.0024
	H_2O	24.2	24,600	40.6	24,600	-
1/1 H_2O/Xylidine	SO_2	1	-	0.05	0.95	0.42[**]
	H_2O	24.2	70.3	35.3	59.2	-
	Xylidine	-	8.4	0.4	8.8	-
6.5 M Slurry[***]	SO_2	1	-	0.05	0.95	6.5
CaO ($CaCO_3$)	H_2O	24.2	16.4	40.6	-[****]	
	CaO	-	0.95	-	0.95	
6.5 M Slurry[***]	SO_2	1	-	0.05	0.95	3.2
MgO ($MgCO_3$)	H_2O	24.2	24.8	35.0	14.0	
	MgO	-	1.64	-	1.64	

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[*] Scrubber solution temperature is 50°C

[*] Partial pressure of incoming SO_2 is 2.28 mm (0.3%)

[*] Partial pressure of effluent SO_2 is 0.114 mm (150 ppm)

[**] Moles/liter solution

[***] System contains 6.5 moles of oxide per liter of water

[****] Solid $CaSO_3$ only is removed from effluent

to reduce the SO_2 vapor pressure to very low values. In the extreme case of neutral water, there is a very low concentration of SO_2 (0.0024 M) associated with an SO_2 partial pressure of 150 ppm at 50°C. As long as the entering scrub water has a concentration of SO_2 that is lower than this value, water is also capable, from an equilibrium standpoint, of attaining the desired effectiveness; very large volumes are required, however. The xylidine/water system (Sulfidine process) can also be used for reducing the SO_2 content to the desired level; the capacity of this system is not high, however.

An analysis of the presence of CO_2 in the systems discussed in the foregoing shows that a very low level of CO_2 is dissolved. Although alkaline solutions are commonly added to scrubber systems, the circulating scrubber solution is usually slightly acidic due to prior absorption of SO_2; the acidic conditions thus account for the low level of CO_2 solubility.

A number of the other processes, e.g., the I.C.I.-Basic Aluminum Sulfate, Magnesium Oxide, Howden-I.C.I., Magnesium Hydroxide, Mitsubishi Simplified Lime, and the Mitsubishi Lime, use magnesium or calcium oxide or hydroxide slurries as scrubbing media. In these systems, the formation of solid carbonates is an important consideration as regards the equilibria with SO_2. The systems are, however, also theoretically capable of reducing the SO_2 content of flue gas to 150 ppm.

3. Sample Calculation

In order to clarify the significance of the data in Table 2 and also the general procedure used to generate these data, a sample calculation for a 6.5 M ammonia scrubbing solution will now be illustrated. The scrubbing solution at the top of the scrubber is assumed to be at 50°C and in equilibrium with the exit gases containing 150 ppm of SO_2. The 150 ppm value corresponds to a partial pressure of 0.114 mm. A calculation of the equilibria involved shows that a solution with a total ammonia content of 6.5 M will be 4.27 M in SO_2. The partial pressures above this solution will be 77.8 mm H_2O, 0.226 mm NH_3, and 0.114 mm SO_2. The volume of entering flue gas that carries 1 mole of SO_2 into the scrubber at a partial pressure of 2.28 mm (0.3%) will leave the top of the scrubber carrying 0.05 moles of SO_2 at a partial pressure 0.114 mm.

Since 0.114 mm SO_2 corresponds to 0.05 moles stack loss, and the stack losses are proportional to the partial pressures, 77.8 mm H_2O and 0.226 mm NH_3 correspond to a stack loss of 34.1 moles H_2O and 0.10 moles NH_3, respectively.

The solution at the bottom of the scrubber containing 6.5 M total ammonia contains 5.80 M dissolved SO_2 in equilibrium with 0.3% SO_2 in the incoming flue gas. The composition of the solution at the bottom is 55.55 moles H_2O, 6.5 moles NH_3, and 5.80 moles SO_2. Therefore, for each amount of solution containing 0.95 moles SO_2 withdrawn from the scrubber, there is withdrawn 9.1 moles H_2O (55.6 x 0.95/5.8) and 1.1 moles of ammonia (6.5 x 0.95/5.8).

The capacity of the scrubbing solution is determined from the difference in SO_2 concentrations at the top and bottom of the scrubber. The scrubbing solution contains 5.80 moles SO_2/liter H_2O at the bottom of the scrubber and 4.27 moles SO_2/liter H_2O at the top. The difference of 1.5 moles [illegible] amount of SO_2 discharged from the system for each liter of water in the scrubbing solution.

A mass balance shows the quantity of chemicals that must be added for each mole of SO_2 scrubbed. There are 24.2 moles of water in the incoming gas stream (7.25%) while 34.1 moles are lost in the stack and 9.1 moles are withdrawn from the bottom of the scrubber. The difference, 19.0 moles, must be added. There must be an addition of 1.2 moles of NH_3 to make up for the 0.10 mole lost in the stack and the 1.1 moles withdrawn.

C. ECONOMIC ANALYSIS

1. Basis for Analysis

a. General Considerations

The preliminary economic analyses reported herein of processes for removing sulfur dioxide from flue gases of power plants are based on the following general considerations.

A power plant of 120,000 kw was selected from a previous cost study.[621*] The cost estimates in the referenced study cover the Fulham-Simon-Carves, the Zinc Oxide, and the Howden-I. C. I. (Cyclic Lime) processes, all of which were evaluated on this program. The earlier work thus provided a sound basis for the present study. The mechanics used in utilizing these data in the present study are illustrated in the detailed economic analysis of the Fulham-Simon-Carves Process (see Section III. C. 2. a.). This detail is not repeated in the sections covering the other processes. Conditions characteristic of the selected power plant are as follows:

- Flue gas contains 0.3 vol-% SO_2
- Removal efficiency is 95% (purified gas would contain 150 ppm SO_2)
- 475,000 tons of coal are consumed per year
- Coal requirement is 1 pound per kilowatt-hour
- Sixty tons of coal are consumed per hour evolving 20 million CFH flue gas at standard conditions of 0° C and 760 mm Hg
- Operations are based on a 330-day operating year.

Chemical-reaction yields were assumed to be equivalent to 100% conversion unless specifically indicated otherwise. No allowances were made for in-plant or other losses, such as exit losses in the purified flue gas.

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[*] See bibliography, Part Six, for references.

Chemical consumption and by-product or waste generation, if applicable, were calculated for the treatment of 1 million SCF of flue gas. These quantities can be easily factored to a power plant of any size.

Flue-gas composition is in accordance with the specifications in the program work statement. This information is reproduced below. The quantity of each component contained in 1 million SCF of flue gas is also given.

Component	Vol-%	Quantity Per Million SCF Lb Moles	Lb	Wt-%
N_2	74.9	2086	58,408	70.10
CO_2	14.7	410	18,040	21.65
H_2O	7.25	202	3,636	4.36
O_2	2.8	78	2,496	3.00
SO_2	0.3	8.36	535	0.64
NO_x(As NO)	0.05	1.39	42	0.05
			83,157	99.80
Fly Ash			167	0.20
			83,324	100.00

At a 95% SO_2 removal level, the quantity of SO_2 absorbed per million SCF of flue gas is 7.94 lb moles or 508 lbs.

For purposes of simplification, the following assumptions were made in carrying out the analyses:

- All gaseous components other than water vapor and SO_2 will pass through the absorber(s) unchanged.
- The water vapor content of the gas will change. The exit gas will be saturated with H_2O at the exit or scrubbing temperature.

- The untreated flue gas will be available at 300°F, and its pressure will have to be increased to overcome the pressure drop in the absorption system.
- The effect of fly ash has not been considered.
- The effect of any required gas cooling on plume buoyance and dispersal and the need for any plume reheat have not been considered.

b. Capital Costs

Costs of preparing various types of capital-cost estimates are discussed by Bauman.[649] A tabulation from that source follows:

Costs of Preparing Indicated Estimated Types

Estimate Type	Median Cost ($) (Up to $1 Million)	Median Cost ($) (Over $1 Million)
Order-of-Magnitude	1000	4000
Study	2000	5000
Preliminary	7000	16000
Definitive	12000	35000

Only order-of-magnitude estimates were utilized in Phase I. More specifically, fixed-capital type estimates were utilized in which the cost of major purchased process equipment was calculated or determined from established or published data. The additions necessary to arrive at the values of the direct-plant and fixed-capital costs were determined as percentages of the physical-plant cost and the direct-plant cost, respectively. In some cases it was adequate to employ Lang's factors for fixed capital, a procedure which is commonly used in the process industries for order-of-magnitude estimating purposes.[268]

Although these estimating procedures are not considered to be more than ± 30% accurate, they serve adequately since the estimates are used only for obtaining relative costs to determine the feasibility of utilizing various aqueous scrubbing techniques. The major scrubbing equipment is quite similar in most of the processes. The most important variance in equipment requirements is associated with absorbent regeneration, recovery of sulfur in a salable form (S, SO_2, H_2SO_4), and in the supporting chemical-plant complex - if required.

The factors for fixed capital for three general processes, as derived by Lang, are as follows:

Process	Factor
Solid	3.10
Solid-fluid	3.63
Fluid	4.74

Thus,

$$I_F = EL$$

where: I_F = fixed-capital investment
E = purchased equipment cost
L = Lang's factor

The 4.74 factor for fluid processes was applied in Phase I of this work. Justification for this selection follows.

These estimate types, as well as many others, appear frequently in the cost literature. Aries and Newton[647] has been a very popular source of cost information for many chemical engineers. The method in the referenced publication, described as Fixed-Capital Estimate, Method 2, was adapted for use on this project. A breakdown of the capital cost items considered by Aries and Newton follows.

Item	Factor
Purchased equipment	1.00
Installation labor	0.25
Foundations & platforms	0.18
Piping	0.86
Instrumentation	0.05 to 0.30
Insulation	0.08
Electrical	0.10 to 0.15
Buildings	0.30
Land & yard improvements	0.10 to 0.15
Utilities	0.40
Physical-Plant Cost	3.32 to 3.67
Engineering & Construction (20% of physical-plant cost)	0.66 0.73
Direct-Plant Cost	3.98 to 4.40
Contractor's Fee (7% dir. plt. cost)	0.28 0.30
Contingency (15% dir. plt. cost)	0.60 0.66
Fixed Capital	4.86 to 5.36

It should be noted that these factors are higher than Lang's (4.74). Even greater variances are found in the cost literature.

Table 3 is presented to illustrate these variances. Column I is derived from the literature[186] and shows average costs as a ratio of purchased equipment for large fluid-processing installations. The over-all fixed capital factor is practically the same as Lang's.

The values shown in columns II, III, and IV were obtained from capital-cost data developed by the Bureau of Mines,[621] all based on plants with a flue-gas volume of 20 million SCFH containing 0.30 vol-% SO_2, and assuming 90% removal of the SO_2. These also are factored estimates, and reference is made in the paper to data from Aries and Newton[647] and others. The fixed capital factors are substantially lower for all three processes than for Lang's. This observation is not critical, however, since they compare well with each other.

TABLE 3

FACTORED FIXED CAPITAL ESTIMATES

ITEM	I	II	III	IV	V
	Haselbarth & Berk	Field, *et al.*			Modified Lang
	Large Fluid Process	Nonregenerative Limestone Process	Ammoniacal Liquor Process	Regenerative Sodium Sulfite Process	Fluid Process
Purchased Equipment	1.00	1.43	1.43	1.43	1.00
Erection Labor	0.43				0.25
Foundations & Platforms					0.18
Piping	0.76	0.72	0.67	0.60	0.76
Instruments	0.19	0.05	0.05	0.05	0.15
Insulation	-	-	-	0.01	0.08
Electrical	0.10	0.05	0.05	0.05	0.10
Buildings	0.23	0.30	0.30	0.30	0.25
Land & Yard Improvement	0.14	0.13	0.13	0.10	0.13
Utilities	0.57	0.11	0.10	0.11	0.40
Receiving, Shipping & Storage	0.24	Misc. 0.11	Misc. 0.11	Misc. 0.11	-
Physical-Plant Costs	3.66	2.90	2.84	2.76	3.30
Engineering & Construction	0.48	0.75	0.74	0.72	0.66
Direct Plant Cost	4.14	3.65	3.58	3.48	3.96
Contractor's Fee	In Eng. & Const.	-	-	-	0.19
Contingency	0.62	0.35	0.34	0.33	0.59
Fixed Capital Costs	4.76	4.00	3.92	3.81	4.74

Many more variances in fixed capital factors (as a percent of purchased equipment cost) can be cited from the literature. The examples given, however, should suffice to indicate the importance of having common bases whenever order-of-magnitude estimates are to be compared with each other. The 4.74 fixed capital factor was selected for Phase I of this project. Volumn V of Table 3 indicates the individual values used.

Working capital usually does not exceed 10-15% of fixed capital. In the Phase I effort of this program, the equivalent of 10% of fixed capital was assigned as working capital.

The sum of the fixed capital cost and the working capital provided the total investment used in the cost estimates of Phase I. The capital cost in terms of dollars per kilowatt generating capacity was considered for each process evaluation.

It is important to remember that the capital investments obtained according to this factored order-of-magnitude method should not be construed as absolute values. They are to be used only to indicate the relative investment costs of the processes under consideration in Phase I. Comparison of these capital investments with others appearing in the literature should be made with extreme care due to the large variation in the magnitude of factors being used in order-of-magnitude cost estimates.

The capital investments in the Bureau of Mines[621] costs were adjusted using the Chemical Engineers' Plant Cost Index.[13] In a typical case, the cost of the major items installed (from the Bureau of Mines report) was divided by 1.43 to obtain the purchased items cost. This value was updated from 1957 to 1967 by increasing the cost by 12.4%.

Preliminary capital-cost estimates made in Phase III on candidate processes were done in a more accurate manner in accordance with the requirements set forth in the program work statement.

c. Operating Costs

The operating costs include all of the direct, indirect, and fixed charges which generally occur in manufacturing operations. The selection of these cost elements is straightforward. However, assignment of unit values to the cost elements is done on a uniform basis in all of the operating-cost estimates. In other words, labor rates, cost of power per kwh, etc., are the same in all estimates in order to simplify the task of evaluating the relative economics of the various processes. A wide variation of values has been assigned by different workers to these cost elements; some of these were determined by actual costs and others were estimated on the basis of past experience. For the purpose of this program, it is only necessary to select realistic values for a hypothetical situation or location. A brief treatment of these cost elements follows.

(1) Direct Costs

(a) Raw Materials, Processing Chemicals, and Catalysts

The costs of these materials have been obtained from standard current sources*, such as the Oil, Paint and Drug Reporter, (OPDR) or from direct quotations. The initial purchase of catalysts, if any, should be capitalized and listed in the plant investment. Only replacement purchases are considered as part of the operating cost. The raw material prices used in the operating cost estimates are shown in Table 4.

(b) Direct Labor

The annual wage of hourly workers is based on 2000 hours. Actually, slightly less than 2000 hours per man-year are charged to direct labor, with holidays, etc., charged to payroll burden. Wage rates vary with the industry and locality. A rate of $3.00 per hour is used in these estimates.

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*The use of the term "current prices" throughout this report refer to OPDR prices as of February, 1968.

TABLE 4

RAW MATERIAL PRICES

All prices obtained from the Oil, Paint and Drug Reporter, February 5, 1968, unless otherwise noted.

Raw Material	Price, Dollars
Ammonia, anhydrous	60 per ton
Ammonium sulfate	31 per ton
Calcium sulfate	0[a]
Calcium sulfite	0[a]
Chlorine	0.0325 per lb
Coke	19 per ton[b]
Hydrazine, anhydrous	2.95 per lb[c]
Lime	15.50 per ton
Limestone, 100 mesh	10 per ton[d]
Magnesium oxide, 95%	61 per ton
Magnesium sulfate	2.45 per 100 lbs
Manganese sulfate, 75%	100 per ton
Oleum, 20%	34.90 per ton
Ozone	0.105 per lb[e]
Soda ash	1.60 per 100 lbs
Sodium sulfate	0[a]
Sulfur	38 per long ton
Sulfur dioxide, liquid	0.0345 per lb
Sulfuric acid, 100%	33.40 per ton
Xylidine	0.45 per lb[f]
Zinc oxide	0.1525 per lb

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a. Waste products assumed at no value.

b. Bibliography reference 653.

c. Olin Mathieson.

d. United Lime Division, Flintkote Co.

e. Bibliography reference 424.

f. DuPont (mixed xylidines).

(c) Operating Supervision

With first-line supervision receiving approximately 25% more than direct labor, an annual rate (salary) of $7,800 is assigned for this cost element. The plant or area superintendent rate is $12,000 per year. The quantity of manpower required, both direct labor and supervision, is estimated for each process under consideration.

(d) Maintenance

Maintenance materials, labor, and supervision are grouped in this cost element. Due to lack of adequate data, the total annual cost of maintenance is set at 5% of the fixed capital investment.

(e) Plant Supplies

Plant supplies are equivalent to 15% of maintenance cost.

(f) Utilities

Utility unit costs are extremely variable in practice and are usually controlled by the plant location and size. The following unit costs were used:

Utility	Cost in Dollars
Steam, M lb	0.50
Heat credits & debits, MM Btu	0.50
Power, kwh	0.006
Raw water, M gal	0.10
Recirculated water, M gal	0.05
Fuel oil, gallon	0.10

(2) Indirect Costs

(a) Payroll Burden

This account covers social security, workmen's compensation, vacations and holidays, contributions to pensions, life insurance and profit-sharing, etc. Consequently, the cost of these fringe benefits is rising steadily and is usually between 15 and 25% of base labor costs. In this work, this cost was shown as 20% of total base labor.

(b) Plant Overhead

The cost of maintaining service functions such laboratory, purchasing, warehousing, engineering, etc., was not individually estimated. Plant overhead was considered to be 50% of labor, maintenance, and supplies.

(c) Packaging and Shipping

These costs were not considered in Phase I.

(d) Waste Disposal

This cost was set[57] at 20 mills per ton mile assuming a maximum haulage of 200 miles, or $4 per dry ton. Transporting waste shorter distances would not affect this cost significantly since handling costs remain constant.

(3) Fixed Costs

(a) Depreciation

The following depreciation information issued as guide-lines by the U. S. Treasury Department is applicable to this project:

• Electrical utility (steam producing plant)	28 years
• Chemical plant	11 years
• Factory buildings	45 years

Although the SO_2 removal equipment will represent additions to power plants, it is doubtful that the useful life of this process equipment would be 28 years. The 11-year period for a chemical plant is probably more realistic for SO_2 removal systems. For simplicity, a 10-year straight-line depreciation which ignores the 45-year write-off on buildings was applied to the fixed capital.

(b) Taxes

A value of 2% of the fixed capital investment has been used in this project.

(c) Insurance

Although a small item, 1% of fixed capital investment was employed to cover plant insurance costs.

An operating cost estimate summary was completed for each of the processes evaluated. These are presented in the respective sections in which the processes are considered.

(d) Cost of Capital

Although the interest cost associated with borrowing capital can be an appreciable operating cost item (typically 8% interest in today's market), this cost item was not included in deriving process operating costs in this study, so that said derived costs are somewhat low due to this exclusion.

d. Profitability

The profitability of each process was considered. A simplified approach was applied for this part of the analysis. The commonly used indexes, such as payout time, return on investment, etc., were not applied. The data are presented simply as a loss or profit in terms of dollars per ton of coal burned and mills per kwh generated at various levels of by-product sales (when applicable).

The magnitude of by-product credits applied to the operating costs can severely affect the profitability of a process. In some cases, the by-products would have a definite impact on the market and on the economy of the United States.

The various by-products produced in these systems are ammonium sulfate, calcium sulfite, calcium sulfate, sulfur, dilute sulfuric acid, magnesium sulfate, sulfur dioxide, sodium sulfate, and anhydrous hydrazine. Conversion of even a small part of the SO_2 emissions from fossil-fuel, power-generating plants to any of these by-products would provide huge quantities of materials.

Several of these by-products have substantial value in today's market. These include: ammonium sulfate, sulfuric acid, sulfur, sulfur dioxide, and anhydrous hydrazine. However, their ultimate value could be seriously affected by the large tonnages which would be produced by the removal of SO_2 from flue gases. The rest of the by-products listed were considered to be waste materials with no value; in addition, a cost is associated with their disposal.

A discussion of the market considerations of the by-products follows.

(1) Ammonium Sulfate

Ammonium sulfate was the major nitrogen fertilizer in the United States from 1923 to 1947.[655] Most of it was produced from coke oven by-product ammonia and sulfuric acid. Since that time it has been replaced in its No. 1 position by ammonium nitrate and more recently by anhydrous ammonia. The relatively low nutrient content of ammonium sulfate has been the major reason for its reduced acceptance in the fertilizer market in the U. S. A. However, it is still the leading nitrogen fertilizer in world-wide areas of relatively low agricultural development.

Production capacity of anhydrous ammonia increased at a steady rate in the late 1950's; however, the most dramatic increase in capacity has occurred since 1964. The capacity of synthetic ammonia plants in the U. S. A. in 1964 was 7,838 M short tons with a projected increase to 17,246 M short tons by January 1968. This great expansion was due to the technological improvements in equipment, resulting in the construction of very large ammonia plants; the effect has been a very significant reduction in production costs. Over 75% of the ammonia produced in the United States today is used in fertilizer. It is used not only as a fertilizer intermediate but is now the leading direct-application nitrogen fertilizer in the United States, due mainly to its low cost.

The total production of ammonium sulfate in the United States in 1963 was 1,823,000 tons. A 120-megawatt power plant would generate enough SO_2 in its flue gas to produce 83,000 tons per year of ammonium sulfate; a 1400 megawatt station, the plant size designated for Cases I and II in Phase III of this study, would produce 622,500 tons per year of ammonium sulfate, or one-third of the annual U.S. production.

It is evident that production of ammonium sulfate from the SO_2 available in the flue gas of several 1400 megawatt power plants would severely upset the ammonium sulfate market. Thus, this by-product cannot be considered as a desirable one based on present conditions, especially when it is the only or the major by-product in a process.

Perhaps a reasonable assumption is that ammonium sulfate could capture a part of the fertilizer market now served by anhydrous ammonia if their price relationship improved. The nutrient content (nitrogen) of ammonia is 82.3% whereas ammonium sulfate contains 21.2%. One unit of nitrogen, which is equivalent to 20 lb of nutrient, costs twice as much in ammonium sulfate as in anhydrous ammonia at today's prices of $31 per ton for ammonium sulfate and $60 per ton for ammonia:

	In NH_3	In $(NH_4)_2SO_4$
Units of nutrient, per ton	82.3	21.2
Fertilizer cost, $ per ton	60	31
Cost per unit, $	0.73	1.46

Thus, to compete with ammonia on the basis of nutrient content, ammonium sulfate would have to sell for $15.50 per ton when the price for anhydrous ammonia is $60 per ton. On this basis, any reduction in anhydrous ammonia price would mean a decrease in the ammonium sulfate price. These price relationships are also affected by geographical location and on specific situations. The total net cost of the nutrient applied to the farmer's soil is probably the determining factor affecting the market price for which ammonium sulfate would have to be sold to be competitive with anhydrous ammonia.

The world-wide market is also a factor since ammonium sulfate is still a major fertilizer in Asia and Europe. Shipping costs, however, would affect the economics. As a matter of interest, however, a recent newsletter[73] announced the sale of 2.25 million metric tons of Japanese ammonium sulfate valued at $69.6 million to mainland China. This is equivalent to 2.475 million short tons at $28.12 per ton.

It is apparent that assignment of credit to ammonium sulfate produced as a by-product in a SO_2 removal system must be done with care. It is unlikely that an adequate market would exist for the large tonnages of ammonium sulfate which could be produced from this source. In this connection it should be noted that the recovery of SO_2 from flue gas in systems which produce ammonium sulfate does not provide a compound which is valuable for its sulfur content. Ammonium sulfate used as fertilizer is valuable primarily for its nitrogen content; although sulfur is a plant nutrient, its function as a component of ammonium sulfate as fertilizer is of secondary importance.

(2) Sulfur and Sulfur Dioxide

Over 70% of the sulfuric acid produced in the United States has been from elemental sulfur. In 1962 the production capacity as 100% acid was 26,000 M tons. Actual production as 19,000 M tons of which 13,000 M tons were produced from elemental sulfur.

Sulfur production in 1961 was 7,200 M long tons of which 5,300 M long tons were derived from native sulfur. The latter quantity is equivalent to more than 18,000 M tons of sulfuric acid. The availability of naturally occurring brimstone has been severely reduced during recent years. This shortage has resulted in cutbacks in sulfuric acid production in some cases. Sulfur producers have found it necessary to ration the sulfur supply during the past year. This situation has resulted in a rapid rise in the price of crude sulfur from approximately $25 per long ton in 1965 to the current price of $42 per long ton. It has also created renewed interest in finding new sources of sulfur for sulfuric acid production.

The recovered SO_2 could be liquefied as shown in the cost estimates; it could also be converted at the power plant site to sulfuric acid or reduced to elemental sulfur depending on the economics in the local situation. Conversion to sulfuric acid would probably provide the most economic route.

(3) Anhydrous Hydrazine

Anhydrous hydrazine is a by-product in two of the processes included in this study. Since a dilute aqueous solution of hydrazine is the absorbing medium in these processes, the hydrazine can either be recycled or withdrawn as a by-product. The quantity of anhydrous hydrazine removed from the system can be regulated; the specific quantity would be controlled by the anhydrous hydrazine market existing at that time.

Hydrazine is marketed as anhydrous hydrazine, 64.0% aqueous hydrazine (hydrazine monohydrate), 54.5% aqueous hydrazine (85% hydrazine monohydrate), and 35% hydrazine. It is also available in the form of various salts.

(4) Calcium Sulfate

Gypsum, calcium sulfate, dihydrate, is used extensively in the manufacture of wallboard, and thus is directly dependent on the building industry. Lesser quantities are used in making plaster, cement, in soil and water conditioning (purification and clarification), and in the beer industry for pH control. The bulk rate for 97% pure gypsum is $4.25 to $4.50 per ton, at the mill. Anhydrous calcium sulfate is valued at $24/ton, in bulk, F. O. B. mill, but the consumption of this material is relatively small, the chief use involving water clarification. The present brief discussion will therefore be restricted to a consideration of the gypsum market.

The following table shows the world production of gypsum during the period 1960-1962:[656]

	Production, M Short Tons		
	1960	1961	1962
North America	16,445	16,135	16,753
South America	452	542	584
Europe	24,130	26,135	26,720
Asia	3,946	3,843	4,291
Africa	933	982	934
Australia/New Caledonia	651	681	683
	46,560	48,320	49,965

The gypsum market has been notably stable.

Several of the processes which have been considered for the removal of SO_2 from flue gases afford gypsum as a product. However, in many cases (e.g., in the Howden-I.C.I. process), the product is contaminated with fly ash and cannot be credited. In the Mitsubishi Lime process a high purity product is obtained. Thus, in this process the gypsum produced was initially considered not as a waste material, but as a by-product with value. The Phase III evaluation, however, showed a dim forecast for marketing pure gypsum in the United States.

2. Detailed Economic Analysis

a. Fulham-Simon-Carves Process

(1) Process Description

The Fulham-Simon-Carves process involves the scrubbing of flue gas with an aqueous solution of ammonium salts, including the sulfite, bisulfite, and thiosulfate. Gas works liquor (an aqueous solution containing ammonia and hydrogen sulfide) or synthetic ammonia is added to the circulating scrubber liquor at a rate corresponding to the rate of sulfur dioxide absorption, and a portion of the liquor is continuously removed for product recovery. The latter involves a preliminary filtration to remove fly ash, followed by an autoclaving step in which the clear liquor is heated in the presence of sulfuric acid to convert bisulfite to sulfate and elemental sulfur. After the withdrawal of molten sulfur from the autoclave the aqueous ammonium sulfate solution is concentrated in a vacuum evaporator, and the precipitated crystalline solid separated by centrifugation, and dried. A flow diagram for the Fulham-Simon-Carves process is shown in Figure 1.

(2) Process Reactions

The reactions shown below apply to the case where gas-works liquor which contains hydrogen sulfide is used as the source of ammonia. When synthetic ammonia is used, the reactions which show the formation of ammonium thiosulfate in the scrubber and the subsequent reaction of the material with ammonium bisulfite in the autoclave are not applicable. As will be indicated, only synthetic ammonia is considered in this study.

Scrubber:

$$NH_3 + H_2O + SO_2 \longrightarrow NH_4HSO_3$$

$$2\,NH_3 + H_2O + SO_2 \longrightarrow (NH_4)_2SO_3$$

$$(NH_4)_2SO_3 + 1/2\ O_2 \longrightarrow (NH_4)_2SO_4$$

$$2\,H_2S + 2\,NH_4HSO_3 + 2\,(NH_4)_2SO_3 \longrightarrow 3\,(NH_4)_2S_2O_3 + 3\,H_2O$$

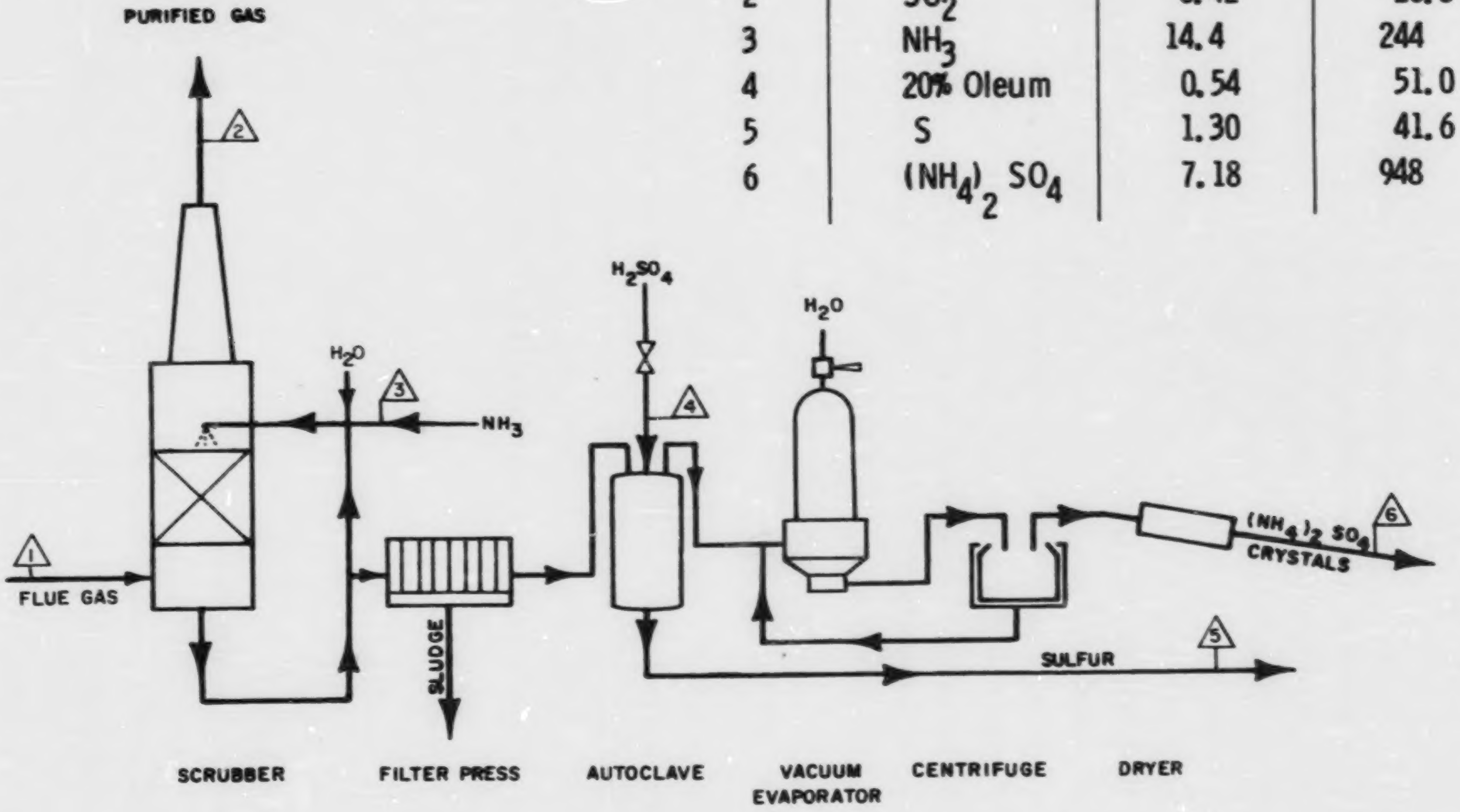
Autoclave:

$$2\,NH_4HSO_3 + (NH_4)_2S_2O_3 \xrightarrow{H_2SO_4} 2\,(NH_4)_2SO_4 + 2\,S + H_2O$$

$$2\,NH_4HSO_3 + (NH_4)_2SO_3 \xrightarrow{H_2SO_4} 2\,(NH_4)_2SO_4 + S + H_2O$$

Reactant Chemicals Per Million SCF Flue Gas Processed

△ Stream	Component	Lb Moles	Lbs.
1	SO_2	8.36	535
2	SO_2	0.42	26.8
3	NH_3	14.4	244
4	20% Oleum	0.54	51.0
5	S	1.30	41.6
6	$(NH_4)_2SO_4$	7.18	948


PURIFIED GAS
2
1
FLUE GAS
H_2O
3
NH_3
SLUDGE
H_2SO_4
4
H_2O
$(NH_4)_2SO_4$ CRYSTALS
6
5
SULFUR
SCRUBBER
FILTER PRESS
AUTOCLAVE
VACUUM EVAPORATOR
CENTRIFUGE
DRYER

FULHAM - SIMON - CARVES PROCESS : FLOW DIAGRAM

Figure 1

(3) Availability of Ammonia

For many years ammonia was obtained commercially as a by-product in the manufacture of coke and gas from coal. This was the situation when the Fulham-Simon-Carves process was developed some thirty years ago. Although some ammonia is still produced in the U.S. in this manner, the most important method now is the Haber process which involves synthesis from nitrogen and hydrogen.

In the United States, most of the by-product ammonia is produced in coke-oven plants. This ammonia is recovered as ammonium sulfate, ammonia liquor, and/or ammonium phosphates. In 1961, 51 plants produced sulfate; 10 plants, ammonia liquor; 3 plants, diammonium phosphate; and 1 plant, monoammonium phosphate.[655]

In 1964, the synthetic ammonia production capacity was 7,838 M short tons of ammonia with a projection of a 17,246 M short-ton capacity in 1968. Production in 1964 was as follows:[651]

	M Short Tons of NH_3
Synthetic, anhydrous	7,508.5
Synthetic, aqueous	62.9
By-product, as $(NH_4)_2SO_4$	175.3
By-product, as liquor	16.3
By-product, as phosphates	11.8

It is not likely that the by-product ammonia now converted to ammonium sulfate would be available as an absorbent for the removal of SO_2 from flue gas. Most of the ammonium sulfate is produced at steel mills and is used to solve a waste pickle-liquor disposal problem; the ammonia is reacted with the waste pickle liquor to produce ammonium sulfate. It will be shown in the following section that the quantity of by-product ammonia liquor available (16.3 thousand short tons in 1964) would not be adequate for the removal of SO_2 from the flue gas generated by one small existing power plant. For this reason, the Fulham-Simon-Carves process using by-product ammonia as an absorbent was not considered. The economic evaluation which follows was therefore based on the use of anhydrous ammonia.

(4) Chemical Requirements and By-Product Yields

Field, et al.[621] used pilot-plant data which were factored for a 20 million SCFH system designed to remove 90% of the SO_2 from flue gas containing 0.3 vol-% SO_2. The quantities of reactants and by-products were based on the use of anhydrous ammonia and not gas works by-product ammoniacal liquor. In the calculations shown herein, a purified flue gas containing 150 ppm of SO_2 will require 95% removal of the SO_2. Although ammonium thiosulfate is not formed when using anhydrous ammonia, the addition of sulfuric acid to the autoclave is still required to convert the ammonium sulfite/bisulfite to ammonium sulfate and sulfur.

Table 5 shows the raw material and by-product requirements for treating one million SCF of gas. Data for three different sized plants, viz., 20 million SCFH, 0.5 million SCFM and 2.5 million SCFM, are also shown in the table. The latter two plant sizes were evaluated in Phase III. These quantities are based on the assumption of full utilization of ammonia, with no allowance for ammonia loss in the treated flue gas. Ammonia losses reported in the pilot-plant operations were 3 to 8% of the make-up ammonia. Ammonia losses of only 0.3 to 0.4% of make-up have also been reported in a pilot-plant operation.[673]

It is evident that the 16,300 short tons of by-product ammonia available in 1964[651] is not sufficient to satisfy the requirements of any of the plants which were considered.

The theoretical quantities of reactant chemicals involved with the treatment of 1 million SCF gas are also shown on the flow diagram, Figure 1.

(5) Cost Estimate

(a) Capital Costs

The capital cost estimate of the Fulham-Simon-Carves process in the Bureau of Mines report contained the following information:

Fixed capital	$4,495,800
Working capital	449,600
Total Investment:	$4,945,400

TABLE 5

FULHAM-SIMON-CARVES PROCESS USING ANHYDROUS AMMONIA: CHEMICAL REQUIREMENTS & BY-PRODUCT YIELDS

	Quantity per Million SCF Flue Gas		Tons per Year		
Raw Materials	Lb Mole	Lb	20 Million SCFH Flue Gas	0.5 Million SCFM Flue Gas	2.5 Million SCFM Flue Gas
SO_2 (flue gas)	7.94	508	40,230	60,350	301,730
NH_3 (anhyd.)	14.36	244	19,325	28,990	144,940
Oleum, 20%	0.54	51	4,040	6,060	30,300
By-Products					
$(NH_4)_2SO_4$	7.18	947	75,000	112,500	562,500
S	1.3	42	3,325	4,990	24,940

The cost of major items installed is $1,637,240 of this total. Dividing this value by 1.43 provides the purchased equipment cost, or $1,144,900. In this case, the fixed capital cost, $4,495,800, is 3.92 times the purchased equipment cost. The fixed capital cost in the present work was taken as 4.74 times the purchased equipment cost. This variance is due to the selection of, and the values applied to, the specific factors making up the fixed cost.

The purchased equipment cost of $1,144,900 in 1957 was corrected to November 1967 costs using the C.E. Plant Index. This amounted to a 12.4% increase, or a total of $1,286,900. This amount was factored according to established standard procedure, resulting in a total investment of $6,704,700, or $55.87/kw capacity. See Table 6.

(b) Operating Costs

The raw material requirements tabulated in Table 5 for the Fulham-Simon-Carves process were based on the assumption that anhydrous ammonia would be used. As mentioned earlier, the supply of by-product ammonia would not be adequate; therefore, operating cost estimates were not prepared on the by-product ammonia system. The total operating cost per year was $3,221,300 or $6.78/ton of coal and 3.39 mill/kwh. See Table 7.

Raw material and chemical costs were based on the data given in Table 5.

Direct labor was assumed to be the same as in the Bureau of Mines report, i.e., 5 men per shift x 4 shifts = 20 men. Supervision was assumed as one foreman per shift and one area superintendent.

The utility requirements given in the Bureau of Mines report were factored to adjust for the change from 90% SO_2 removal to 95%.

Steam:	364,000 M lb per year
Power:	12,236,000 kwh
Make-up Water:	200,000 M gal per year
Circulating Water:	975,000 M gal per year

In the Bureau of Mines study it was assumed that the by-products would be handled in bulk. Costs are not included for bags, labor or bagging equipment. Costs in the present study will similarly be based on bulk materials.

TABLE 6

FULHAM-SIMON-CARVES PROCESS: CAPITAL COST ESTIMATE SUMMARY

	ITEM	FACTOR	COST - $
1.	Purchased Equipment	1.00	1,286,900
2.	Erection Labor	0.25	321,700
3.	Foundation & Platforms	0.18	231,600
4.	Piping	0.76	978,000
5.	Instruments	0.15	193,000
6.	Insulation	0.08	103,000
7.	Electrical	0.10	128,700
8.	Buildings	0.25	321,700
9.	Land & Yard Improvements	0.13	167,300
10.	Utilities	0.40	514,800
	Physical-Plant Cost	3.[illegible]	4,246,700
12.	Engineering & Construction	0.66	849,400
13.	Direct Plant Cost	3.96	5,096,100
14.	Contractor's Fee	0.19	244,500
15.	Contingency	0.59	759,300
16.	Fixed Capital Cost	4.74	6,099,900
17.	Working Capital, 10%	0.47	604,800
	Total Investment	5.21	6,704,700
18.	Capital Requirements		
	$/kw capacity	55.87	

TABLE 7

FULHAM-SIMON-CARVES PROCESS OPERATING COST ESTIMATE SUMMARY

Fixed Capital Cost: $6,099,900

	ITEM	TOTAL $	%
1.	Raw Materials & Chemicals	1,300,500	40.37
2.	Direct Labor	120,000	3.73
3.	Supervision	43,200	1.34
4.	Maintenance, 5% of Fixed Capital	305,000	9.47
5.	Supplies, 15% of Maintenance	45,800	1.42
6.	Utilities	324,200	10.06
7.	Other	-	-
8.	TOTAL DIRECT COST	2,138,700	66.39
9.	Payroll Burden, 20% of 2 & 3	32,600	1.01
10.	Plant Overhead, 50% of 2, 3, 4 & 5	257,000	7.98
11.	Pack & Ship	-	-
12.	Waste Disposal	-	-
13.	Other	-	-
14.	TOTAL INDIRECT COST	289,600	8.99
15.	Depreciation, 10 % Fixed Capital/Yr	610,000	18.94
16.	Taxes, 2% of Fixed Capital	122,000	3.79
17.	Insurance, 1% of Fixed Capital	61,000	1.89
18.	Other	-	-
19.	TOTAL FIXED COST	793,000	24.62
20.	TOTAL OPERATING COST	3,221,300	100.00

21.	COST: $/Ton of Coal	6.78
22.	Mill/kwh	3.39

23. BY-PRODUCT CREDIT (SEE FIGURE 2)

(c) Profitability

Figure 2 indicates the profitability of the Fulham-Simon-Carves process on the basis of selling the sulfur produced at $33.00 per long ton, with ammonium sulfate offered at variable prices.

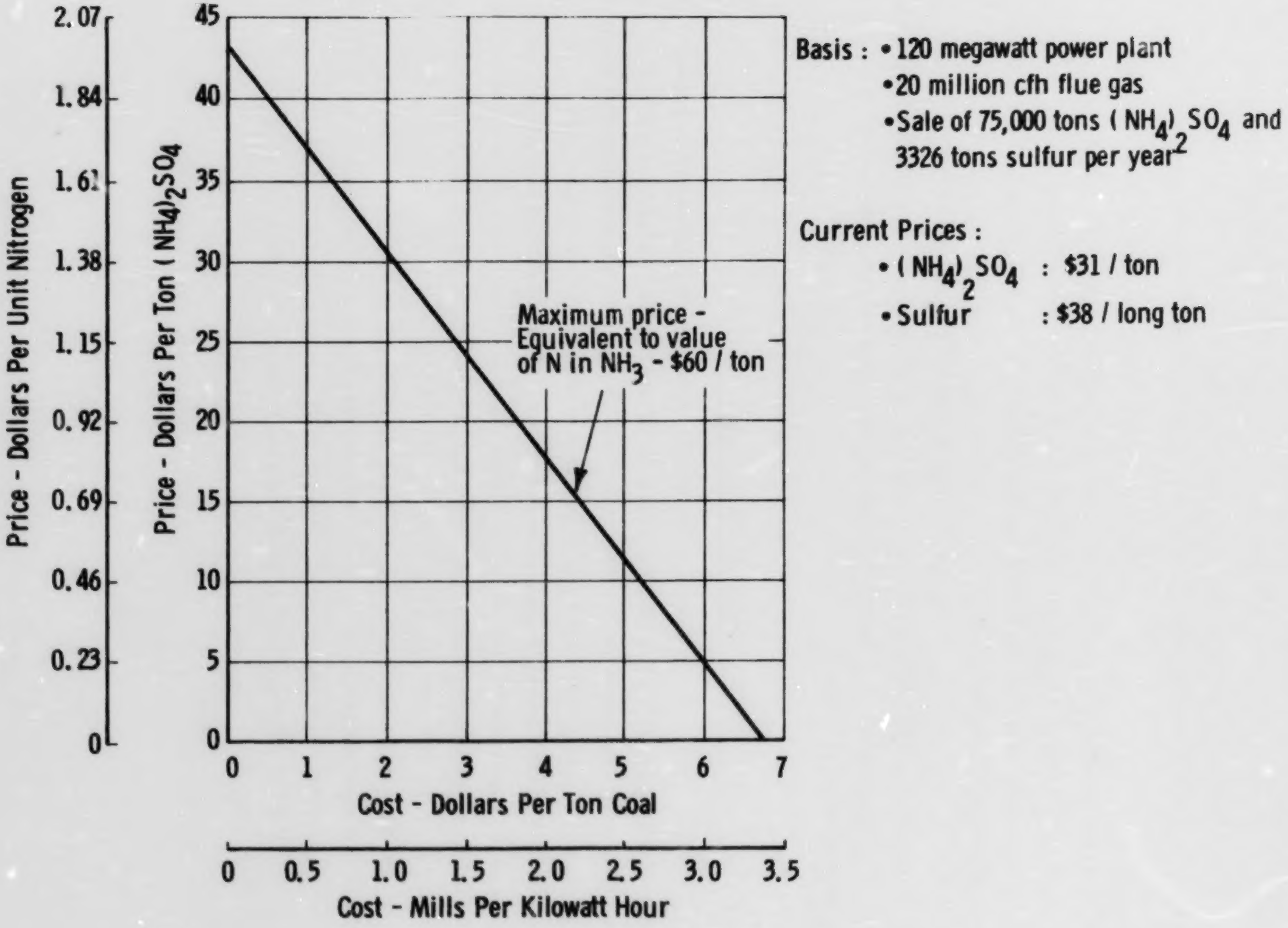
On this basis, the estimates indicate that the cost of removing SO_2 from the flue gas of a 120,000 kilowatt plant may be in the range of $4-5 per ton of coal or 2.0 - 2.5 mills per kilowatt hour. It is probable that more detailed cost estimates applied to larger power plants would indicate a reduction of this cost.

With reference to the effect of stack losses on operating cost and profitability, it is of interest to note that each 1% of makeup ammonia equivalent lost through the stack would increase the operating cost by $0.024 per ton of coal burned.

b. Showa-Denko Ammoniacal Process

(1) Process Description

The Showa-Denko Ammoniacal process involves the scrubbing of flue gas with an aqueous solution of ammonium salts. In this process, make-up ammonia is injected into the flue gas to reduce corrosion upstream of the scrubber, whereas in the Fulham-Simon-Carves process ammonia is introduced directly into the scrubber. The scrubber itself is similar to that employed in the Fulham-Simon-Carves process. A portion of the circulating liquor is continuously removed for product recovery. The off-stream liquor is filtered to remove fly ash, treated with ammonia to convert any bisulfite present to sulfite, and then oxidized with air to convert the sulfite to sulfate. The ammonium sulfate solution is then concentrated in an evaporator-crystallizer, and the precipitated crystalline solid separated by centrifugation, and dried. A flow diagram for the Showa-Denko Ammoniacal process is shown in Figure 3.

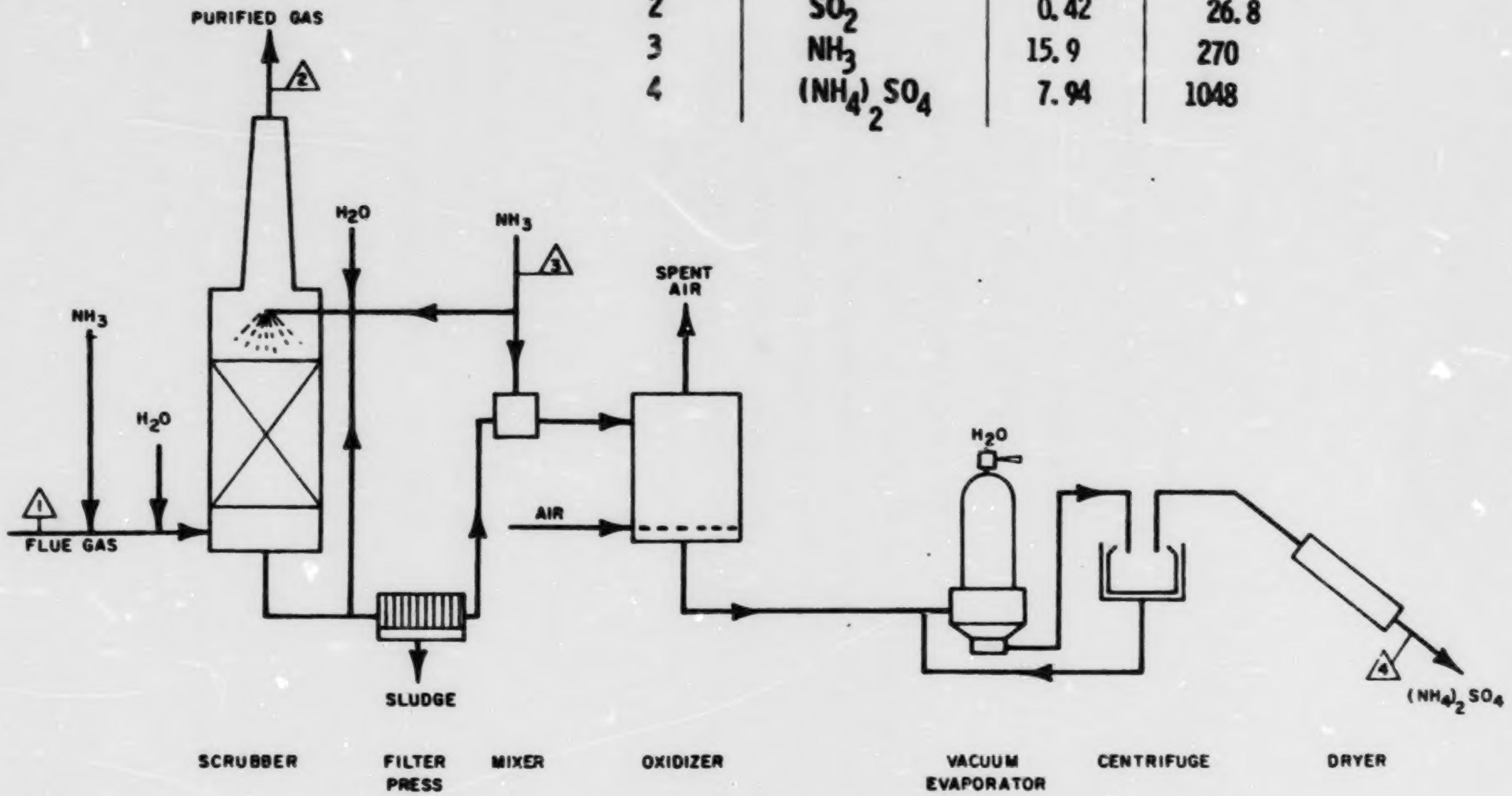


FULHAM-SIMON-CARVES PROCESS USING ANHYDROUS AMMONIA : PROFITABILITY

Figure 2

Reactant Chemicals Per Million SCF Flue Gas Processed

△ Stream	Component	Lb Moles	Lbs
1	SO_2	8.36	535
2	SO_2	0.42	26.8
3	NH_3	15.9	270
4	$(NH_4)_2SO_4$	7.94	1048


PURIFIED GAS
2
H_2O
NH_3
3
SPENT AIR
NH_3
H_2O
1
FLUE GAS
AIR
H_2O
SLUDGE
4
$(NH_4)_2SO_4$
SCRUBBER
FILTER PRESS
MIXER
OXIDIZER
VACUUM EVAPORATOR
CENTRIFUGE
DRYER

SHOWA - DENKO AMMONIACAL PROCESS : FLOW DIAGRAM

Figure 3

(2) Process Reactions

Scrubber:

$$NH_3 + H_2O + SO_2 \longrightarrow NH_4HSO_3$$

$$2\,NH_3 + H_2O + SO_2 \longrightarrow (NH_4)_2SO_3$$

$$(NH_4)_2SO_3 + 1/2\ O_2 \longrightarrow (NH_4)_2SO_4$$

Mixer:

$$NH_4HSO_3 + NH_3 \longrightarrow (NH_4)_2SO_3$$

Oxidizer:

$$(NH_4)_2SO_3 + 1/2\ O_2 \longrightarrow (NH_4)_2SO_4$$

The available data indicate no pertinent difference between the absorption system used in the Fulham-Simon-Carves process and that in the Showa-Denko process when anhydrous ammonia is used. Therefore, it is reasonable to assume that raw material requirements and by-product output would be the same. Equipment requirements would vary only in the oxidation step of the by-product liquor stream. This equipment variance, which affects capital cost, direct labor, and utility charges, will be indicated in the cost estimates which follow.

(3) Cost Estimate Detail

Since very little data are available for this process, it was assumed that the Fulham-Simon-Carves process plant, with minor modifications, could be used for the Showa-Denko Ammoniacal system.

(a) Capital Costs

The major change for this system relative to the Fulham-Simon-Carves system is the elimination of the autoclave step and the addition of a facility for air-oxidation of the sulfite sidestream removed for by-product recovery. The following equipment would not be needed:

Autoclaves - 2
H_2SO_4 storage tank
Oleum storage tank
Liquor pump to autoclave - 2
H_2SO_4 pumps - 2

Although details were not available concerning the oxidation equipment required, the following were assumed to be needed:

- 5000-gal aeration tank
- Air compressor

The reduction in purchased equipment was estimated as $81, 300. Table 8 summarizes the capital cost estimate for this process and shows a total investment of $6, 281, 100, or $52. 34/kw capacity.

(b) Operating Costs

The raw material requirements for the Showa-Denko process are listed in Table 9. It should be noted that anhydrous ammonia is the only raw material required and that ammonium sulfate is the only by-product.

Direct labor is reduced by one man per shift relative to that required in the Fulham-Simon-Carves process due to elimination of the autoclave operation. Supervision requires one foreman per shift and one area superintendent.

Utility requirements are the same as those needed in the Fulham-Simon-Carves process except for a reduction in steam cost due to elimination of the autoclave.

Steam:	229, 000 M lb per year
Power:	12, 236, 000 kwh per year
Make-up Water:	200, 000 M gal per year
Circulating Water:	975, 000 M gal per year

The total operating cost per year was estimated at $3, 012, 100, or $6. 34/ton of coal and 3. 17 mill/kwh. See Table 10 for details.

(c) Profitability

Figure 4 shows the profitability of this process, which indicates a cost of $3-4 per ton of coal or 1. 2-2. 0 mills per kilowatt hour.

TABLE 8

SHOWA-DENKO PROCESS: CAPITAL COST ESTIMATE SUMMARY

	ITEM	FACTOR	COST - $
1.	**Purchased Equipment**	1.00	1,205,600
2.	**Erection Labor**	0.25	301,400
3.	**Foundation & Platforms**	0.18	217,000
4.	**Piping**	0.76	916,300
5.	**Instruments**	0.15	180,800
6.	**Insulation**	0.08	96,400
7.	**Electrical**	0.10	120,600
8.	**Buildings**	0.25	301,400
9.	**Land & Yard Improvements**	0.13	156,700
10.	**Utilities**	0.40	482,200
11.	**Physical-Plant Cost**	3.30	3,978,400
12.	**Engineering & Construction**	0.66	795,700
13.	**Direct Plant Cost**	3.96	4,774,100
14.	**Contractor's Fee**	0.19	229,100
15.	**Contingency**	0.59	711,300
16.	**Fixed Capital Cost**	4.74	5,714,500
17.	**Working Capital, 10%**	0.47	566,600
	Total Investment	5.21	6,281,100

18. **Capital Requirements**
$/kw capacity 52.34

TABLE 9

SHOWA-DENKO AMMONIACAL PROCESS:
CHEMICAL REQUIREMENTS & BY-PRODUCT YIELDS

	Quantity per Million SCF Flue Gas		Tons per Year		
Raw Materials	Lb Mole	Lb	20 Million SCFH Flue Gas	0.5 Million SCFM Flue Gas	2.5 Million SCFM Flue Gas
SO_2 (flue gas)	7.94	508	40,230	60,350	301,730
NH_3 (anhyd.)	15.88	270	21,380	32,070	160,350
By-Product					
$(NH_4)_2SO_4$	7.94	1048	83,000	124,500	622,500

TABLE 10

SHOWA-DENKO PROCESS: OPERATING COST ESTIMATE SUMMARY

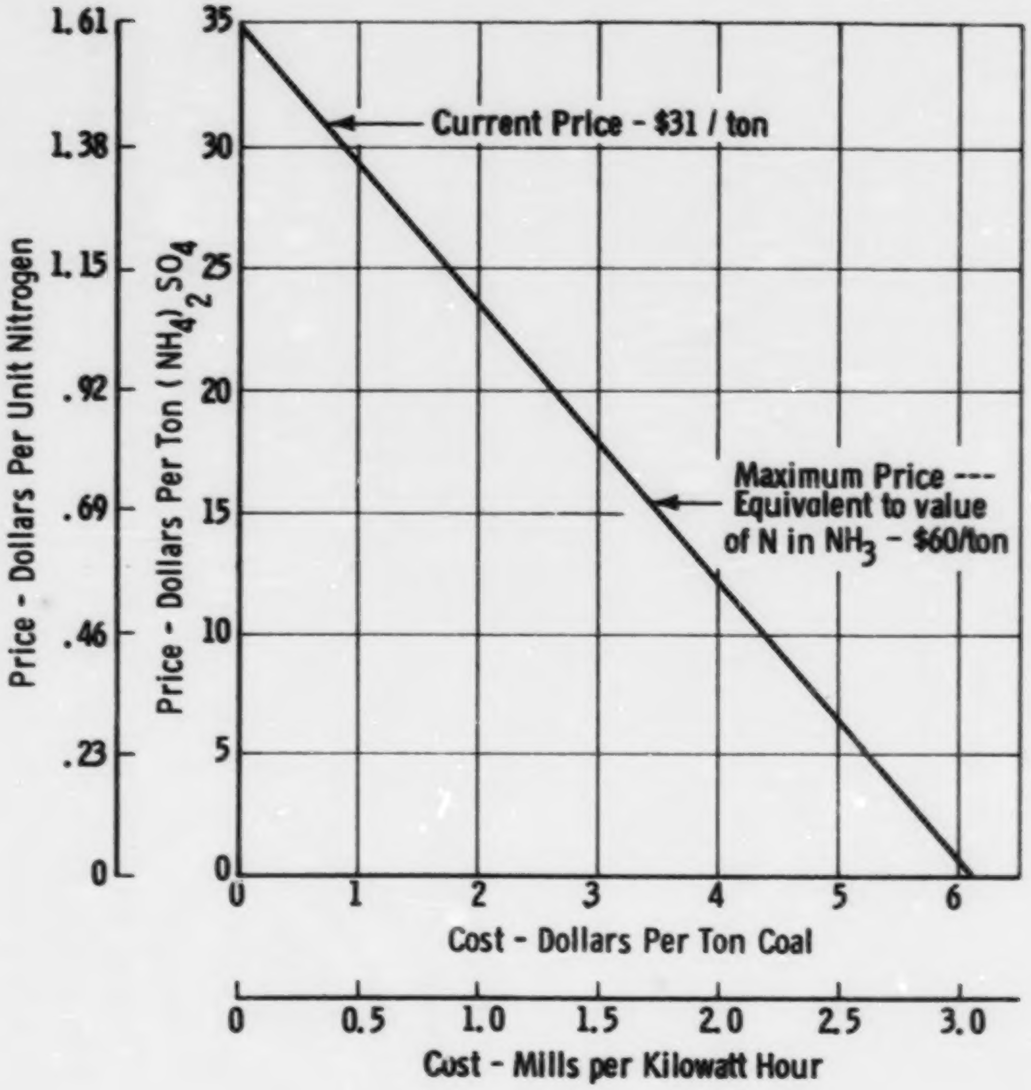
Fixed Capital Cost: $5,714,500

	ITEM	TOTAL $	%
1.	Raw Materials & Chemicals	1,283,000	42.60
2.	Direct Labor	96,000	3.19
3.	Supervision	43,200	1.43
4.	Maintenance, 5% of Fixed Capital	285,700	9.49
5.	Supplies, 15% of Maintenance	42,900	1.42
6.	Utilities	256,700	8.52
7.	Other	-	-
8.	TOTAL DIRECT COST	2,007,500	66.65
9.	Payroll Burden, 20% of 2 & 3	27,800	0.92
10.	Plant Overhead, 50% of 2, 3, 4 & 5	233,900	7.77
11.	Pack & Ship	-	-
12.	Waste Disposal	-	-
13.	Other	-	-
14.	TOTAL INDIRECT COST	261,700	8.69
15.	Depreciation, 10 % Fixed Capital/Yr	571,500	18.97
16.	Taxes, 2% of Fixed Capital	114,300	3.80
17.	Insurance, 1% of Fixed Capital	57,100	1.90
18.	Other	-	-
19.	TOTAL FIXED COST	742,900	24.66
20.	TOTAL OPERATING COST	3,012,100	100.00

21. COST: $/Ton of Coal 6.34

22. Mill/kwh 3.17

23. BY-PRODUCT CREDIT (SEE FIGURE 4)



Basis :
- 120 megawatt power plant
- 20 million cfh flue gas
- Sale of 83,000 tons of $(NH_4)_2SO_4$ per year

SHOWA-DENKO AMMONIACAL PROCESS : PROFITABILITY

Figure 4

c. Cominco Process

(1) Process Description

The Cominco process involves the scrubbing of flue gas with an aqueous solution of ammonium salts, and in this respect is similar to the Fulham-Simon-Carves and Showa-Denko Ammoniacal processes. However, in the Cominco process, the off-stream liquor is treated with sulfuric acid, which results in the liberation of sulfur dioxide, and in the formation of ammonium sulfate. The latter compound is isolated in the manner described in connection with the other ammonia-based processes mentioned above. A flow diagram of the Cominco process is shown in Figure 5.

(2) Process Reactions

Scrubber:

$$\begin{aligned} NH_3 + H_2O + SO_2 &\longrightarrow NH_4HSO_3 \\ 2\,NH_3 + H_2O + SO_2 &\longrightarrow (NH_4)_2SO_3 \\ (NH_4)_2SO_3 + 1/2\,O_2 &\longrightarrow (NH_4)_2SO_4 \end{aligned}$$

Acidifier:

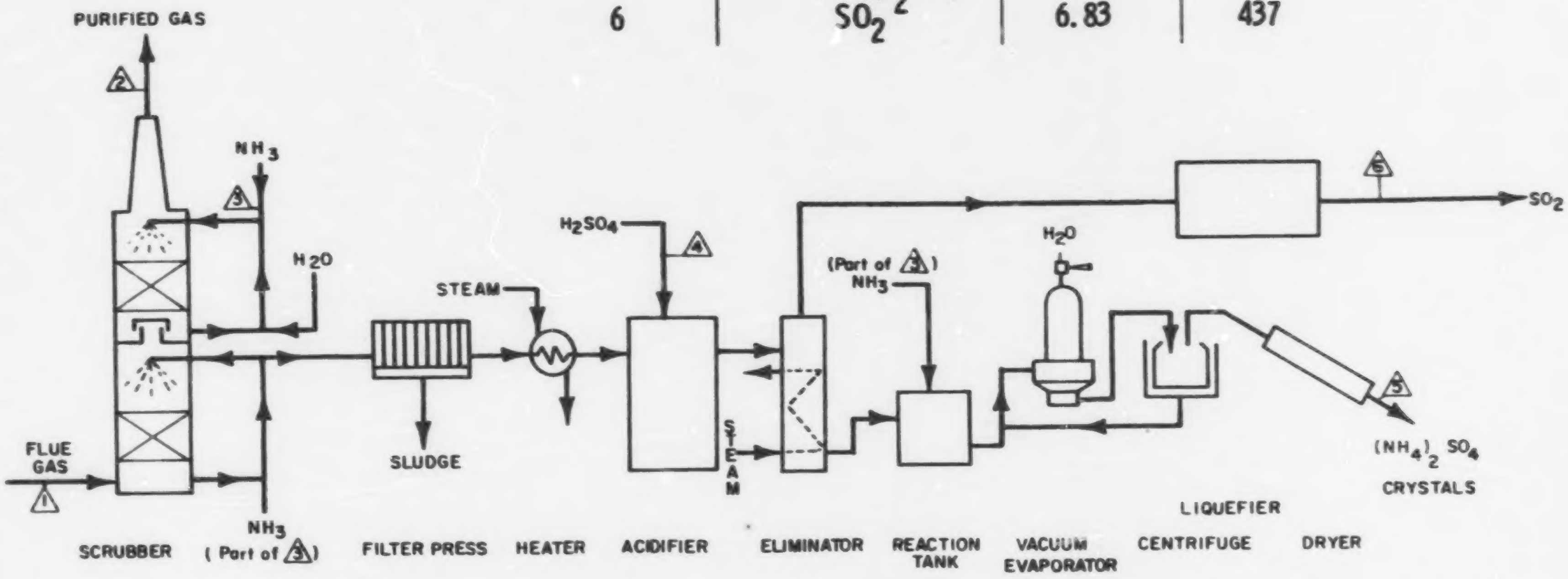
$$\begin{aligned} 2\,NH_4HSO_3 + H_2SO_4 &\longrightarrow (NH_4)_2SO_4 + 2SO_2\uparrow + 2H_2O \\ (NH_4)_2SO_3 + H_2SO_4 &\longrightarrow (NH_4)_2SO_4 + SO_2\uparrow + H_2O \end{aligned}$$

(3) Chemical Requirements and By-Product Yields

Table 11 lists the raw material requirements and by-product yields for treating one million SCF of flue gas by the Cominco process. In addition, the annual requirements for three different sized plants, i.e., 20 million SCFH, 0.5 million SCFM, and 2.5 million SCFM, respectively, are shown. The raw material quantities allow for oxidation of 14% of the SO_2 to SO_3; this oxidation affects: (1) the quantity of ammonia needed to satisfy the reactions, and (2) the relative quantities of the by-products, ammonium sulfate and SO_2. The 14% value selected is the same as that used in the Zinc Oxide process evaluation[621] and is also essentially in agreement with the results of pilot-plant studies based on the Cominco process.[673] Stack and in-plant losses have not been included in the data shown in Table 11.

Reactant Chemicals Per Million SCF Flue Gas Processed

△ Stream	Component	Lb Moles	Lbs
1	SO_2	8.36	535
2	SO_2	0.42	26.8
3	NH_3	9.05	154
4	H_2SO_4	3.42	335
5	$(NH_4)_2SO_4$	4.53	597
6	SO_2	6.83	437


PURIFIED GAS
2
NH3
3
H2O
FLUE GAS
1
NH3 (Part of 3)
STEAM
SLUDGE
H2SO4
4
STEAM
(Part of 3) NH3
H2O
6
SO2
5
(NH4)2 SO4 CRYSTALS
SCRUBBER
FILTER PRESS
HEATER
ACIDIFIER
ELIMINATOR
REACTION TANK
VACUUM EVAPORATOR
LIQUEFIER
CENTRIFUGE
DRYER

COMINCO PROCESS : FLOW DIAGRAM

Figure 5

TABLE 11

COMINCO PROCESS:

CHEMICAL REQUIREMENTS & BY-PRODUCT YIELDS

	Quantity per Million SCF Flue Gas		Tons per Year		
	Lb Mole	Lb	20 Million SCFH Flue Gas	0.5 Million SCFM Flue Gas	2.5 Million SCFM Flue Gas
Raw Materials[a]					
SO_2 (flue gas)	7.94	508	40,230	60,350	301,730
NH_3 (anhyd.)	9.05	154	12,195	18,290	91,460
H_2SO_4 (100%)	3.41	335	26,530	39,800	198,980
By-Products					
$(NH_4)_2SO_4$	4.52	597	47,280	70,920	354,600
SO_2	6.83	437	34,610	51,960	259,800

---

[a] Assumes 14% of SO_2 oxidized to SO_3

(4) Cost Estimate Detail

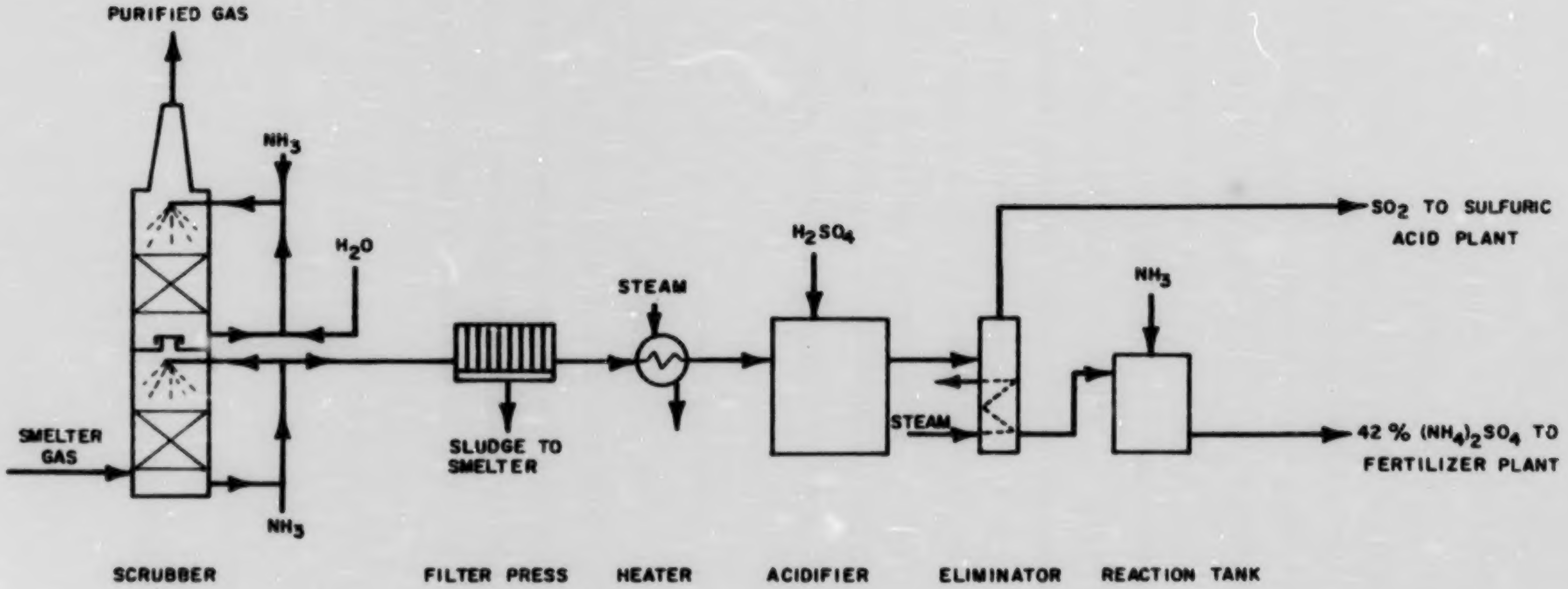
The cost estimates reported previously for the Fulham-Simon-Carves and Showa-Denko Ammoniacal processes were based on the assumption that the same basic equipment, with modifications as needed, could be used for both processes. The Cominco process has been used primarily on high SO_2 content (approximately 6%) waste gases from smelters and other metallurgical operations. There are several variations of the process as used. The basic process, however, consists of: (1) a dual or multi-scrubber system for removal of SO_2; (2) conversion of ammonium bisulfite with sulfuric acid to ammonium sulfate, sulfur dioxide, and water; and (3) stripping the residual SO_2 with steam from the 40% ammonium sulfate solution. The stripped SO_2 is used to produce sulfuric acid in an adjacent plant, while the ammonium sulfate solution is evaporated to produce crystalline material which can be used as a fertilizer.[245] A simplified flow diagram, Figure 6, illustrates the process as applied at The Consolidated Mining and Smelting Company of Canada, Limited, Trail, B. C. An analysis of the process equipment indicated that the equipment used in the Fulham-Simon-Carves process can be adapted, with minor changes, to this process.

(a) Capital Costs

The equipment for the Cominco process to handle removal of 95% of the SO_2 from flue gas in a 120,000 kilowatt power plant can be selected from the equipment used in the other ammonia-based processes. For example, all of the Fulham-Simon-Carves process equipment can be used with the exception of the autoclave. The following additional equipment would also be needed:

- SO_2 liquefaction system
- Acidifier
- Eliminator

An estimate of the purchased equipment cost follows:


PURIFIED GAS
NH$_3$
H$_2$O
SMELTER GAS
NH$_3$
SLUDGE TO SMELTER
STEAM
H$_2$SO$_4$
STEAM
SO$_2$ TO SULFURIC ACID PLANT
NH$_3$
42 % (NH$_4$)$_2$SO$_4$ TO FERTILIZER PLANT
SCRUBBER
FILTER PRESS
HEATER
ACIDIFIER
ELIMINATOR
REACTION TANK

COMINCO PROCESS : FLOW DIAGRAM
(SMELTER GAS)
Figure 6

Fulham-Simon-Carves installed equipment cost -	$1,637,240	
Autoclaves (2)	-91,000	(installed)
SO_2 liquefaction system	+129.500	(installed)
Revised installed equipment cost (1957):	$1,675,740	

Purchased equipment cost	$1,171,800	
Current cost	1,317,000	
Acidifiers (2)	30,000	(purchased)
Eliminators (2)	50,000	(purchased)
Current purchase cost:	$1,397,000	

The estimated total investment is $7,278,400, or $60.65/kw capacity. See Table 12.

(b) Operating Costs

The estimated operating cost is summarized in Table 13, which shows an annual cost of $3,626,900, or $7.64/ton of coal and 3.82 mill/kwh. Raw material costs were based on the quantities shown in Table 11.

Elimination of the autoclave and addition of the other equipment was not expected to affect the labor requirement. Therefore, both the direct labor and supervision are shown as equivalent to the Fulham-Simon-Carves quantities, i.e., 20 operators, 4 shift foremen, and one area superintendent.

Although the steam requirement was reduced by 134,700 M lb per year due to elimination of the autoclave, additional steam amounting to 22,000 M lb per year was needed in the eliminator to strip the residual SO_2 in the liquor. The net reduction in steam compared with the Fulham-Simon-Carves system was 112,700 M lb per year. It was also expected that the SO_2 liquefaction plant would add considerably to the utilities cost. A 3-4 stage compression of SO_2, requiring intercoolers and final condensers, was needed to produce anhydrous liquid SO_2.[194] Aries and Newton[647] indicate a power requirement of 0.002 kwh and 9.0 gallons of water per pound of SO_2 produced. The utilities cost shown in the Fulham-Simon-Carves process would be increased by $830 per year in power costs and $31,000 in water costs. Therefore, the total utilities cost was $299,700 for the Cominco process.

TABLE 12

COMINCO PROCESS: CAPITAL COST ESTIMATE SUMMARY

	ITEM	FACTOR	COST - $
1.	**Purchased Equipment**	1.00	1,397,000
2.	**Erection Labor**	0.25	349,300
3.	**Foundation & Platforms**	0.18	251,500
4.	**Piping**	0.76	1,061,700
5.	**Instruments**	0.15	209,600
6.	**Insulation**	0.08	111,700
7.	**Electrical**	0.10	139,700
8.	**Buildings**	0.25	349,300
9.	**Land & Yard Improvements**	0.13	181,600
10.	**Utilities**	0.40	558,700
11.	PHYSICAL-PLANT COST	3.30	4,610,100
12.	**Engineering & Construction**	0.66	922,000
13.	DIRECT PLANT COST	3.96	5,532,100
14.	**Contractor's Fee**	0.19	265,400
15.	**Contingency**	0.59	824,300
16.	FIXED CAPITAL COST	4.74	6,621,800
17.	**Working Capital, 10%**	0.47	656,600
	TOTAL INVESTMENT	5.21	7,278,400

18. **Capital Requirements**

$/kw capacity 60.65

TABLE 13

COMINCO PROCESS: OPERATING COST ESTIMATE SUMMARY

Fixed Capital Cost: $6,621,800

	ITEM		TOTAL $	%
1.	Raw Materials & Chemicals		1,617,800	44.60
2.	Direct Labor		120,000	3.31
3.	Supervision		43,200	1.19
4.	Maintenance, 5% of Fixed Capital		331,100	9.13
5.	Supplies, 15% of Maintenance		49,700	1.37
6.	Utilities		299,700	8.27
7.	Other		-	-
8.	TOTAL DIRECT COST		2,461,500	67.87
9.	Payroll Burden, 20% of 2 & 3		32,600	0.90
10.	Plant Overhead, 50% of 2, 3, 4 & 5		272,000	7.50
11.	Pack & Ship		-	-
12.	Waste Disposal		-	-
13.	Other		-	-
14.	TOTAL INDIRECT COST		304,600	8.40
15.	Depreciation, 10 % Fixed Capital/Yr		662,200	18.26
16.	Taxes, 2% of Fixed Capital		132,400	3.65
17.	Insurance, 1% of Fixed Capital		66,200	1.82
18.	Other		-	-
19.	TOTAL FIXED COST		860,800	23.73
20.	TOTAL OPERATING COST		3,626,900	100.00
21.	COST: $/Ton of Coal	7.64		
22.	Mill/kwh	3.82		
23.	BY-PRODUCT CREDIT		(SEE FIGURE 7)	

The operating cost, without applying by-product credits, was $7.56 per ton of coal burned, which is somewhat higher than the costs of the other ammonia systems evaluated.

(c) Profitability

Figure 7 illustrates the levels of profitability of this process with by-product sales at various unit prices, with an expected cost of $4-5/ton of coal or 2-2.5 mill/kwh.

d. Cominco Exorption Process

(1) Process Description

The Cominco Exorption process may be regarded as a variation of the Cominco process, in that the off-stream liquor is heated, rather than treated with sulfuric acid, for the liberation of sulfur dioxide. In principle, no ammonium sulfate is produced, and no make-up ammonia is required. However, some oxidation of sulfite to sulfate does occur, particularly during gas scrubbing, and to this extent ammonium sulfate is also isolated. The process was used early in World War II, when ammonia was in short supply. A flow diagram of the Cominco Exorption process is shown in Figure 8.

(2) Process Reactions

Scrubber:

$$NH_3 + H_2O + SO_2 \longrightarrow NH_4HSO_3$$

$$2\,NH_3 + H_2O + SO_2 \longrightarrow (NH_4)_2SO_3$$

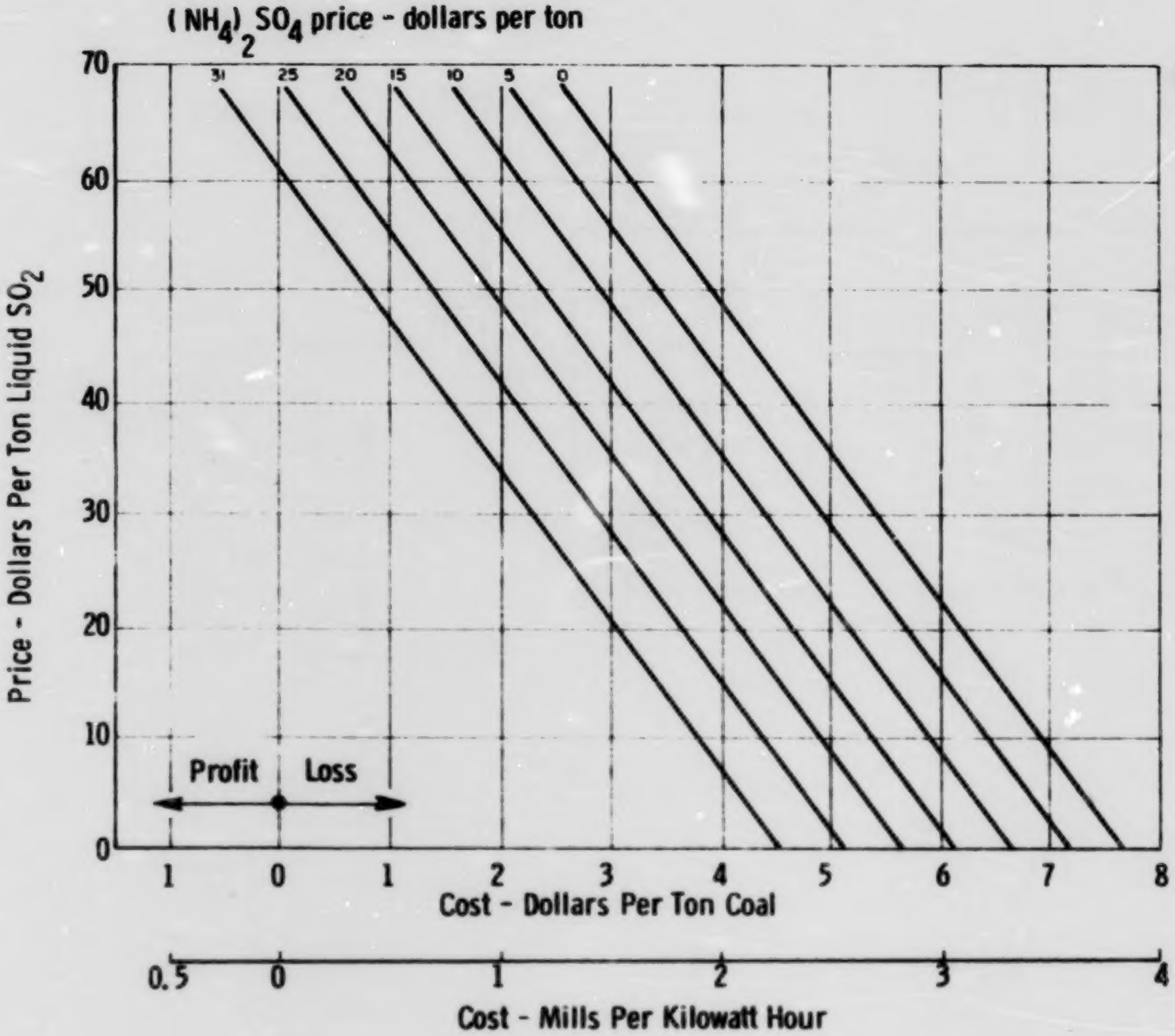
$$(NH_4)_2SO_3 + 1/2\ O_2 \longrightarrow (NH_4)_2SO_4$$

Heater:

$$2\,NH_4HSO_3 \longrightarrow (NH_4)_2SO_3 + SO_2\uparrow + H_2O$$

(3) Chemical Requirements and By-Product Yields

Table 14 shows the raw material needs and by-product production for the Cominco Exorption process.



Basis : •120 megawatt power plant
•20 million cfh flue gas
•Sale of 47,280 tons $(NH_4)_2SO_4$ and
34,610 tons SO_2 per year

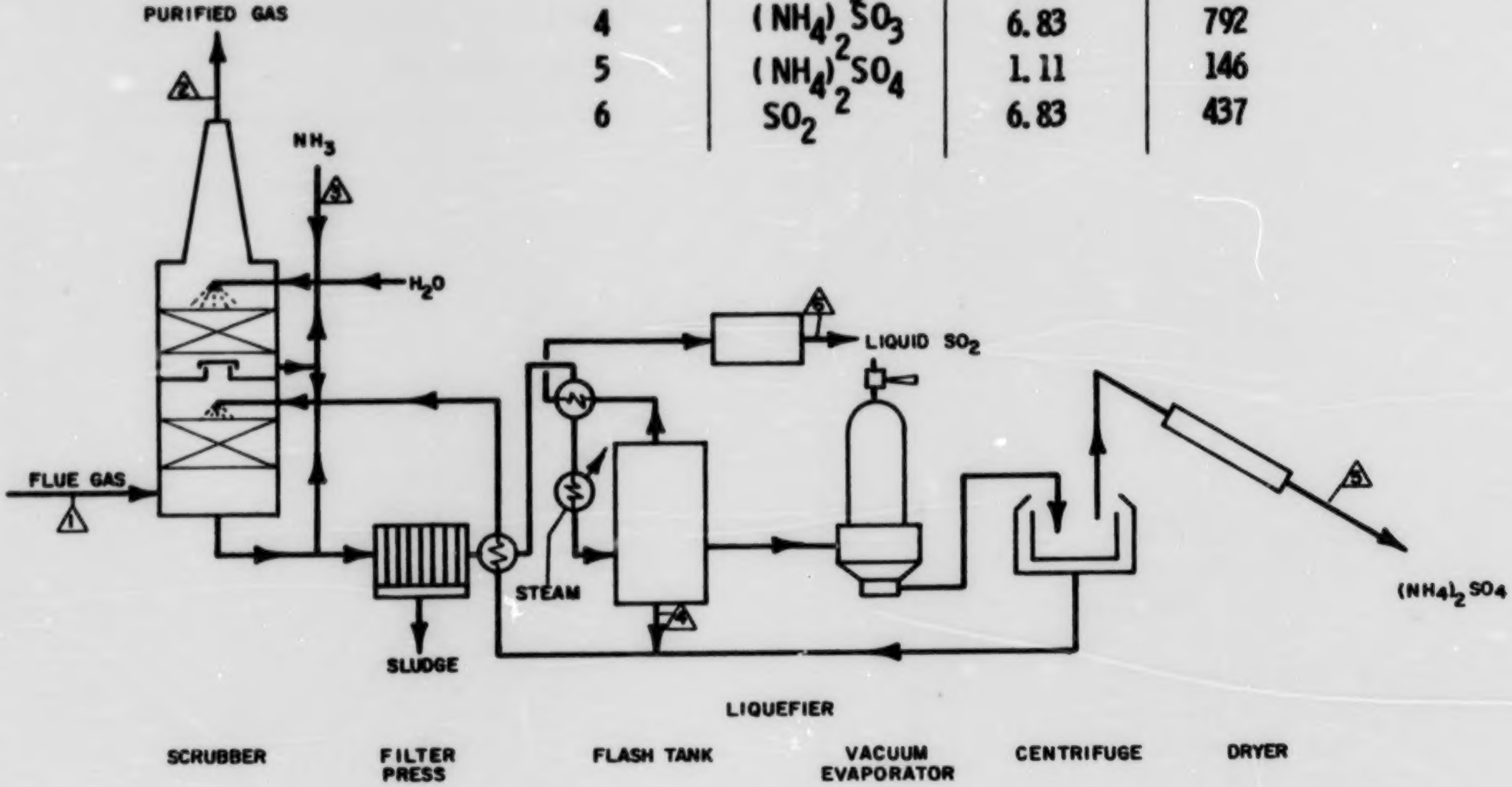
Current Prices :
- Liquid SO_2 : $69 / ton
- $(NH_4)_2SO_4$: $31 / ton

COMINCO PROCESS : PROFITABILITY

Figure 7

Reactant Chemicals Per Million SCF Flue Gas Processed

△ Stream	Component	Lb Moles	Lbs
1	SO_2	8.36	535
2	SO_2	0.42	26.8
3	NH_3	2.22	38.0
4	$(NH_4)_2SO_3$	6.83	792
5	$(NH_4)_2SO_4$	1.11	146
6	SO_2	6.83	437


PURIFIED GAS
2
NH3
3
H2O
FLUE GAS
1
6
LIQUID SO2
STEAM
SLUDGE
4
5
(NH4)2 SO4
LIQUEFIER
SCRUBBER
FILTER PRESS
FLASH TANK
VACUUM EVAPORATOR
CENTRIFUGE
DRYER

COMINCO EXORPTION PROCESS : FLOW DIAGRAM

Figure 8

TABLE 14

COMINCO EXORPTION PROCESS:

CHEMICAL REQUIREMENTS & BY-PRODUCT YIELDS

	Quantity per Million SCF Flue Gas		Tons per Year		
	Lb Mole	Lb	20 Million SCFH Flue Gas	0.5 Million SCFM Flue Gas	2.5 Million SCFM Flue Gas
Raw Materials[a]					
SO_2 (flue gas)	7.94	508	40,230	60,350	301,730
NH_3 (anhyd.)	2.22	38	3,010	4,520	22,580
By-Products					
$(NH_4)_2SO_4$	1.11	147	11,640	17,460	87,300
SO_2	6.83	437	34,610	51,960	259,800

---

[a] Assumes 14% of SO_2 oxidized to SO_3

(4) Cost Estimate

In comparing the flow diagram, Figure 8 , with the flow diagram of the Cominco process, Figure 5 , it will be noted that minor changes in equipment were made. It is also pointed out that the ammonium sulfate system will be reduced in size since the quantity of ammonium sulfate liquor handled and ammonium sulfate crystals recovered was substantially reduced. The effect of this reduction is shown in the following paragraphs.

(a) Capital Costs

The purchased equipment cost of the Cominco process was estimated at $1,397,000. Several equipment changes were needed to convert the system to the Exorption process. The acidifier and eliminator considered in the Cominco process would not be required in the Cominco Exorption process. However, additional required equipment would include two coolers, a heater and flash tank, and a condenser. A reduction in the size of the vacuum evaporator and centrifuge would also be applicable to the Exorption process. Since the daily usage of anhydrous ammonia is substantially reduced, the storage tank was reduced from 229,000 gallons to 35,000 gallons. The net change amounted to +$78,300, resulting in a purchased equipment cost of $1,475,300. The capital cost data are presented in Table 15, showing a total investment of $7,686,300, or $64.05/kw capacity.

(b) Operating Costs

Table 16 summarizes the operating costs for the Exorption process. The annual cost amounts to $2,726,400, or $5.74/ton of coal and 2.87 mill/kwh. The raw material cost is much lower than in the Cominco process since the absorbent is recirculated. Direct labor and supervision costs are assumed to be the same as in the Cominco process.

The Cominco process data also provided the basis for the utilities charges. The following changes were made:

TABLE 15

COMINCO EXORPTION PROCESS: CAPITAL COST ESTIMATE SUMMARY

	ITEM	FACTOR	COST - $
1.	**Purchased Equipment**	1.00	1,475,300
2.	**Erection Labor**	0.25	368,800
3.	**Foundation & Platforms**	0.18	265,600
4.	**Piping**	0.76	1,121,200
5.	**Instruments**	0.15	221,300
6.	**Insulation**	0.08	118,000
7.	**Electrical**	0.10	147,500
8.	**Buildings**	0.25	368,800
9.	**Land & Yard Improvements**	0.13	191,800
10.	**Utilities**	0.40	590,200
11.	PHYSICAL-PLANT COST	3.30	4,868,500
12.	**Engineering & Construction**	0.66	973,700
13.	DIRECT PLANT COST	3.96	5,842,200
14.	**Contractor's Fee**	0.19	280,300
15.	**Contingency**	0.59	870,400
16.	FIXED CAPITAL COST	4.74	6,992,900
17.	**Working Capital, 10%**	0.47	693,400
	TOTAL INVESTMENT	5.21	7,686,300

18. **Capital Requirements**
$/kw capacity 64.05

TABLE 16

COMINCO EXORPTION PROCESS: OPERATING COST ESTIMATE SUMMARY

Fixed Capital Cost: $6,992,900

	ITEM	TOTAL $	%
1.	Raw Materials & Chemicals	180,600	6.63
2.	Direct Labor	120,000	4.40
3.	Supervision	43,200	1.59
4.	Maintenance, 5% of Fixed Capital	349,600	12.82
5.	Supplies, 15% of Maintenance	52,400	1.92
6.	Utilities	756,400	27.74
7.	Other	-	-
8.	TOTAL DIRECT COST	1,502,200	55.10
9.	Payroll Burden, 20% of 2 & 3	32,600	1.20
10.	Plant Overhead, 50% of 2, 3, 4 & 5	282,600	10.36
11.	Pack & Ship	-	-
12.	Waste Disposal	-	-
13.	Other	-	-
14.	TOTAL INDIRECT COST	315,200	11.56
15.	Depreciation, 10 % Fixed Capital/Yr	699,300	25.65
16.	Taxes, 2% of Fixed Capital	139,800	5.13
17.	Insurance, 1% of Fixed Capital	69,900	2.56
18.	Other	-	-
19.	TOTAL FIXED COST	909,000	33.34
20.	TOTAL OPERATING COST	2,726,400	100.00

21. COST: $/Ton of Coal 5.74
22. Mill/kwh 2.87

23. BY-PRODUCT CREDIT (SEE FIGURE 9)

Steam:

Reduction of 17,000 M lbs due to the reduction in the size of vacuum evaporator, ejectors and dryer.

Increase of 758,000 M lbs for the heater requirement.

Net change: +741,000 M lbs.

Power:

Reduction of 477,000 kwh due to reduction in size of centrifuge and dryer.

Water:

Reduction of 731,000 M gal of circulating water due to reduction in the capacity of barometric- and inter-condensers.

Increase of 2,025,000 M gal of circulating water for coolers and condenser.

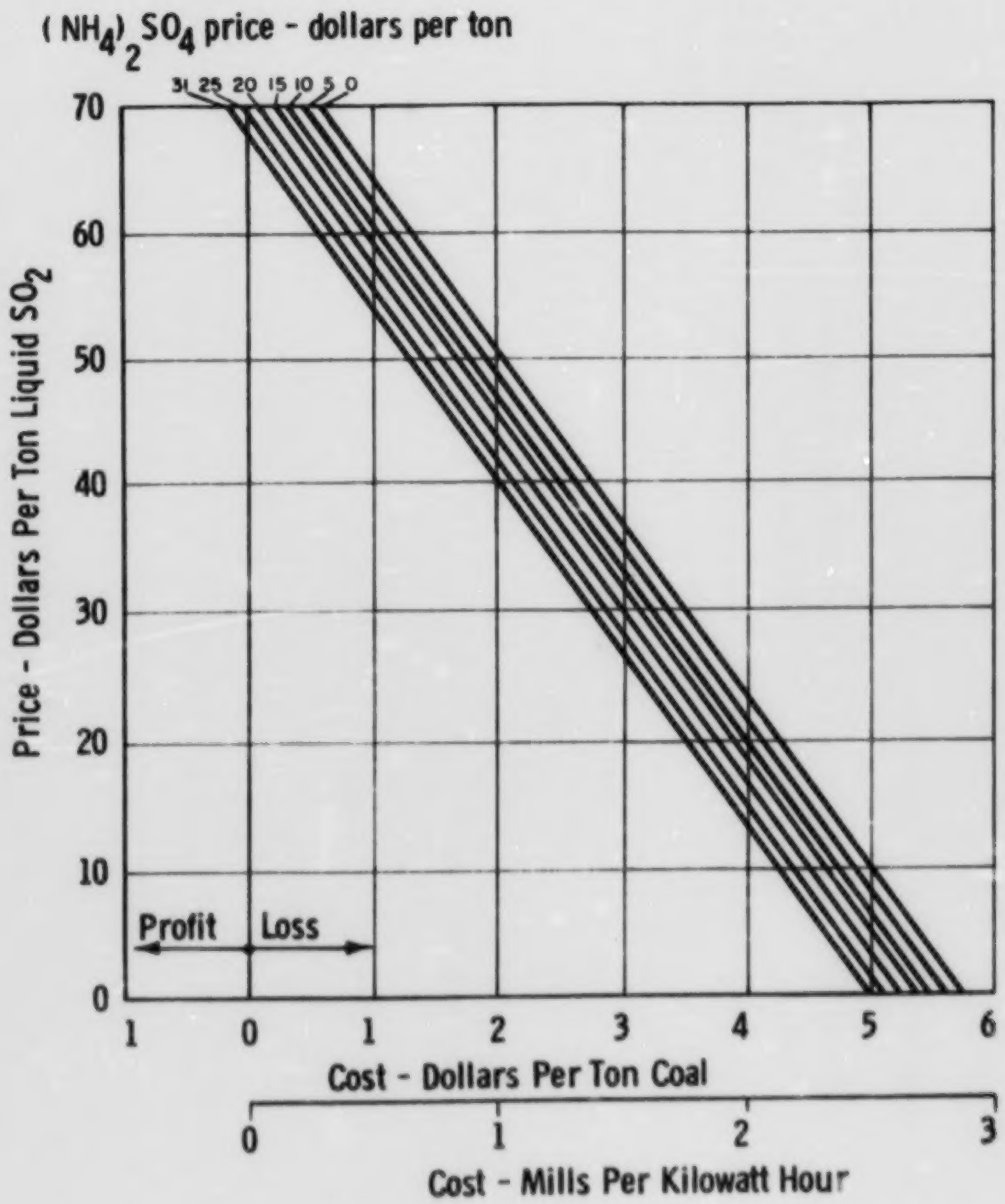
Net change: +1,294,000 M gal.

The utility requirements thus became:

Steam:	1,105,000 M lb per year
Power:	11,759,400 kwh per year
Makeup Water:	200,000 M gal per year
Circulating Water:	2,269,000 M gal per year

(c) Profitability

Figure 9 illustrates the profitability of the operation with the by-products sold at various prices. The anticipated cost is approximately $4/ton of coal or 2 mill/kwh.



Basis :
- 120 megawatt power plant
- 20 million cfh flue gas
- Sale of 11,640 tons $(NH_4)_2SO_4$ and 34,610 tons SO_2 per year

Current Prices :
- Liquid SO_2 : $69 / ton
- $(NH_4)_2SO_4$: $31 / ton

COMINCO EXORPTION PROCESS : PROFITABILITY
Figure 9

e. Zinc Oxide Process

(1) Process Description

In the Zinc Oxide process the flue gas is scrubbed with an aqueous solution of sodium sulfite and sodium bisulfite. Zinc oxide is mixed with the effluent liquor, forming insoluble zinc sulfite. This is filtered, dried, and calcined to produce product sulfur dioxide and zinc oxide, which is returned to the process.

Inasmuch as some oxidation occurs in the scrubber to produce sulfate, which cannot be calcined, the process does include provisions for its removal. The scrubber liquor is treated with insoluble calcium sulfite, and the mixture is passed through a clarifier. The underflow from the clarifier, which contains the calcium sulfite, is acidified with a portion of the product sulfur dioxide, thereby causing the calcium sulfite to dissolve. Calcium ion is thus made available for precipitation as calcium sulfate, which is removed by filtration and discarded. The filtrate is treated with lime to precipitate calcium sulfite, and it is then returned to the clarifier. A flow diagram for the Zinc Oxide process is shown in Figure 10.

(2) Process Reactions

Scrubber:

$$Na_2SO_3 + H_2O + SO_2 \longrightarrow 2\,NaHSO_3$$

$$Na_2SO_3 + 1/2\,O_2 \longrightarrow Na_2SO_4$$

Liming Tank:

$$2\,NaHSO_3 + CaO \longrightarrow Na_2SO_3 + CaSO_3 \downarrow + H_2O$$

Gasifier:

$$CaSO_3 + H_2O + SO_2 \longrightarrow Ca(HSO_3)_2$$

$$Ca(HSO_3)_2 + Na_2SO_4 \longrightarrow 2\,NaHSO_3 + CaSO_4 \downarrow$$

Mixer:

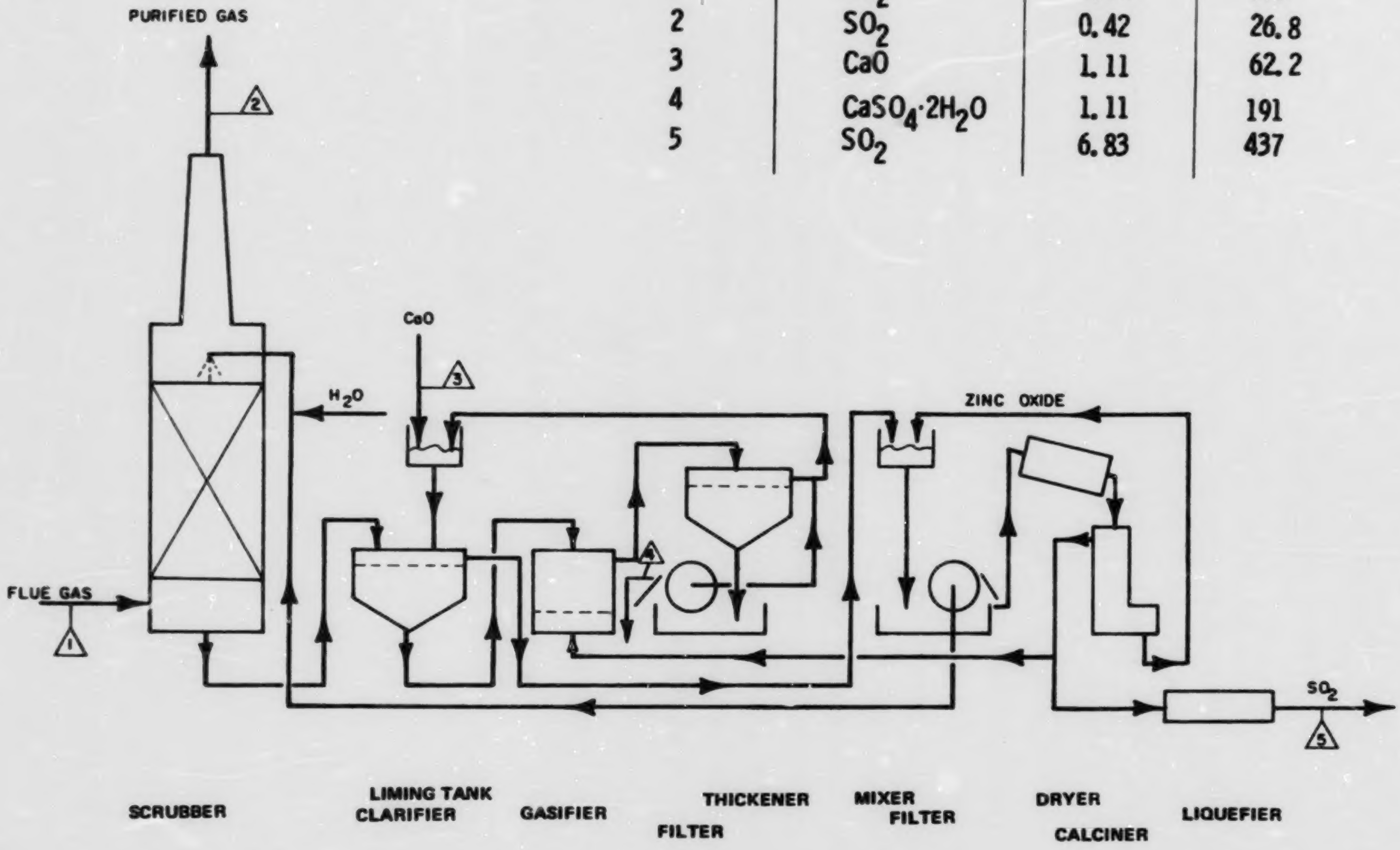
$$2\,NaHSO_3 + ZnO \longrightarrow Na_2SO_3 + ZnSO_3 \downarrow + H_2O$$

Calciner:

$$ZnSO_3 \longrightarrow ZnO + SO_2 \uparrow$$

Reactant Chemicals Per Million SCF Flue Gas Processed

△ Stream	Component	lb-moles	lbs
1	SO_2	8.36	535
2	SO_2	0.42	26.8
3	CaO	1.11	62.2
4	$CaSO_4 \cdot 2H_2O$	1.11	191
5	SO_2	6.83	437


PURIFIED GAS
2
CaO
3
H_2O
ZINC OXIDE
FLUE GAS
1
4
SO_2
5
SCRUBBER
LIMING TANK
CLARIFIER
GASIFIER
THICKENER
FILTER
MIXER
FILTER
DRYER
CALCINER
LIQUEFIER

ZINC OXIDE PROCESS : FLOW DIAGRAM

Figure 10

(3) Chemical Requirements and By-Product Yields

Table 17 indicates the raw material and by-product requirements for treating one million SCF of flue gas by the Zinc Oxide process. A complication which arises with processes in which SO_2 is recovered as such is that of partial oxidation of the SO_2 to sulfate in the gas scrubber. In the case of the Zinc Oxide process this has been estimated by Johnstone and Singh[594] as occurring to the extent of about 10%, and by the Bureau of Mines report[621] as approximately 14%. The latter value was used for the present analysi

Although the Zinc Oxide process is essentially self-contained, various make-up chemicals are required as the result of spray losses in the scrubber and dust losses in the calciner and drier. However, this type of loss will, in general, occur in all of the processes under consideration to about the same degree, and will consequently have little effect on the relative economic ranking of the various processes. For this reason such consistent losses were not considered in the present effort.

(4) Cost Estimate Detail

(a) Capital Costs

The capital cost estimates in the Bureau of Mines report included the following:

Fixed Capital	$2,882,550
Working Capital	288,260
Total Investment:	$3,170,810

These values were adjusted as shown in the cost summary, Table 18, yielding a total investment of $4,430,600, or $36.92/kw capacity.

TABLE 17

ZINC OXIDE PROCESS:

CHEMICAL REQUIREMENTS & BY-PRODUCT YIELDS

	Quantity per Million SCF Flue Gas		Tons per Year		
	Lb Mole	Lb	20 Million SCFH Flue Gas	0.5 Million SCFM Flue Gas	2.5 Million SCFM Flue Gas
Raw Materials					
SO_2 (flue gas)	7.94	508	40,230	60,350	301,730
CaO	1.11	62	4,890	7,340	36,700
By-Products					
SO_2	6.83	437	34,610	51,960	259,800
$CaSO_4$	1.11	191	15,130	22,700	113,480

TABLE 18

ZINC OXIDE PROCESS: CAPITAL COST ESTIMATE SUMMARY

	ITEM	FACTOR	COST - $
1.	Purchased Equipment	1.00	850,400
2.	Erection Labor	0.25	212,600
3.	Foundation & Platforms	0.18	153,100
4.	Piping	0.76	646,300
5.	Instruments	0.15	127,600
6.	Insulation	0.08	68,000
7.	Electrical	0.10	85,000
8.	Buildings	0.25	212,600
9.	Land & Yard Improvements	0.13	110,600
10.	Utilities	0.40	340,100
11.	Physical-Plant Cost	3.30	2,806,300
12.	Engineering & Construction	0.66	561,300
13.	Direct Plant Cost	3.96	3,367,600
14.	Contractor's Fee	0.19	161,600
15.	Contingency	0.59	501,700
16.	Fixed Capital Cost	4.74	4,030,900
17.	Working Capital, 10%	0.47	399,700
	Total Investment	5.21	4,430,600

18. Capital Requirements
$/kw capacity 36.92

(b) Operating Costs

The estimated annual operating costs are listed in Table 19, as $1,874,500, or $3.95/ton of coal and 1.98 mill/kwh. Lime is the only raw material cost shown.

Direct labor amounts to 20 men. Supervision is the same as in previous processes, i.e., four shift foremen and one area superintendent. The utility requirements are as follows:

Steam: 228,000 M lb per year
Power: 3,500,000 kwh per year
Make-up Water: 634,000 gallons
Fuel Oil: 3,611,000 gal per year

Approximately 22,500 tons of wet calcium sulfate cake contaminated with fly ash will be produced. Since it is doubtful that this will have any value, a disposal operating cost should be considered. On the basis of $4 per ton, a waste disposal cost of $90,000 is included in the operating cost.

(c) Profitability

Figure 11 shows the profitability of the Zinc Oxide process as a function of SO_2 selling price. With liquid SO_2 selling for \$20/ton the net cost would be about \$2.50/ton of coal or 1.25 mill/kwh.

The cost of sodium carbonate and zinc oxide losses are not reflected in the operating cost and profitability analysis. The make-up quantities of these chemicals according to the Bureau of Mines report could affect costs, as follows:

585,200 lb/year ZnO = \$89,200
2228 ton/year 58% Na_2CO_3 = 71,300
Added operating cost: \$160,500

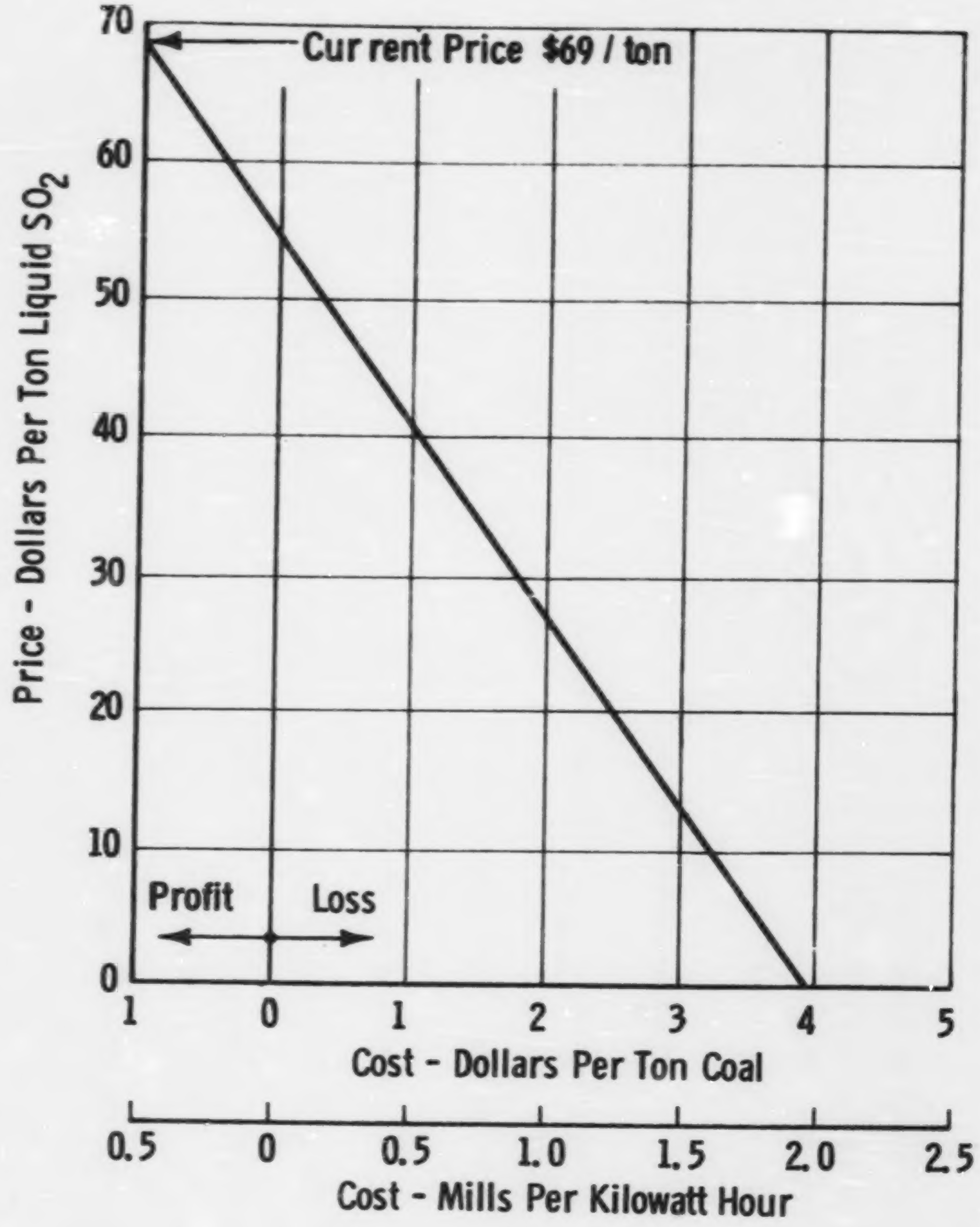
or \$0.34 per ton of coal burned.

TABLE 19

ZINC OXIDE PROCESS: OPERATING COST ESTIMATE SUMMARY

Fixed Capital Cost: $4, 030, 900

	ITEM		TOTAL $	%
1.	Raw Materials & Chemicals		75, 800	4. 04
2.	Direct Labor		120, 000	6. 40
3.	Supervision		43, 200	2. 31
4.	Maintenance, 5% of Fixed Capital		201, 600	10. 76
5.	Supplies, 15% of Maintenance		30, 200	1. 61
6.	Utilities		559, 600	29. 85
7.	Other		-	-
8.	TOTAL DIRECT COST		1, 030, 400	54. 97
9.	Payroll Burden, 20% of 2 & 3		32, 600	1. 74
10.	Plant Overhead, 50% of 2, 3, 4 & 5		197, 500	10. 54
11.	Pack & Ship		-	-
12.	Waste Disposal		90, 000	4. 80
13.	Other		-	-
14.	TOTAL INDIRECT COST		320, 100	17. 08
15.	Depreciation, 10 % Fixed Capital/Yr		403, 100	21. 50
16.	Taxes, 2% of Fixed Capital		80, 600	4. 30
17.	Insurance, 1% of Fixed Capital		40, 300	2. 15
18.	Other		-	-
19.	TOTAL FIXED COST		524, 000	27. 95
20.	TOTAL OPERATING COST		1, 874, 500	100. 00
21.	COST: $/Ton of Coal	3. 95		
22.	Mill/kwh	1. 98		
23.	BY-PRODUCT CREDIT		(SEE FIGURE 11)	



Basis : •120 megawatt power plant
•20 million cfh flue gas
•Sale of 34,656 tons SO_2 per year

ZINC OXIDE PROCESS : PROFITABILITY

Figure 11

f. The Howden-I. C. I. (Cyclic Lime) and Mitsubishi Simplified Lime Processes

(1) Process Description

In the Howden-I. C. I. process, the sulfur dioxide is scrubbed from the flue gas by a neutralization reaction with a slurry containing 5-10% lime or limestone. The actual absorbent in this system is calcium bicarbonate, which is present in solution as the result of the equilibrium reaction with calcium carbonate. A portion of this circulating medium is continually withdrawn and waste calcium sulfite separated as a sludge. Because of the partial oxidation of sulfite to sulfate in the system, calcium sulfate is also present in the waste products.

The Mitsubishi Simplified Lime process is essentially identical with the Howden-I. C. I process, and the following discussion relating to the Howden process is therefore considered to apply to the Mitsubishi process as well. The various Mitsubishi processes are considered further in Sections II, C, 2, r to u.

As indicated in a Bureau of Mines study,[621] lime is preferable to limestone because of its greater reactivity. However, either material is suitable and hence the final choice may be made as the result of the economic factors concerning the particular plant under consideration. A flow diagram of the system is presented as Figure 12.

(2) Process Reactions

Scrubber:

$$SO_2 + Ca(HCO_3)_2 \longrightarrow CaSO_3\downarrow + 2\,CO_2 + H_2O$$

$$CaSO_3\downarrow + 1/2\,O_2 \longrightarrow CaSO_4\downarrow$$

Makeup Tank:

$$CaO + CO_2 \longrightarrow CaCO_3\downarrow$$

and/or

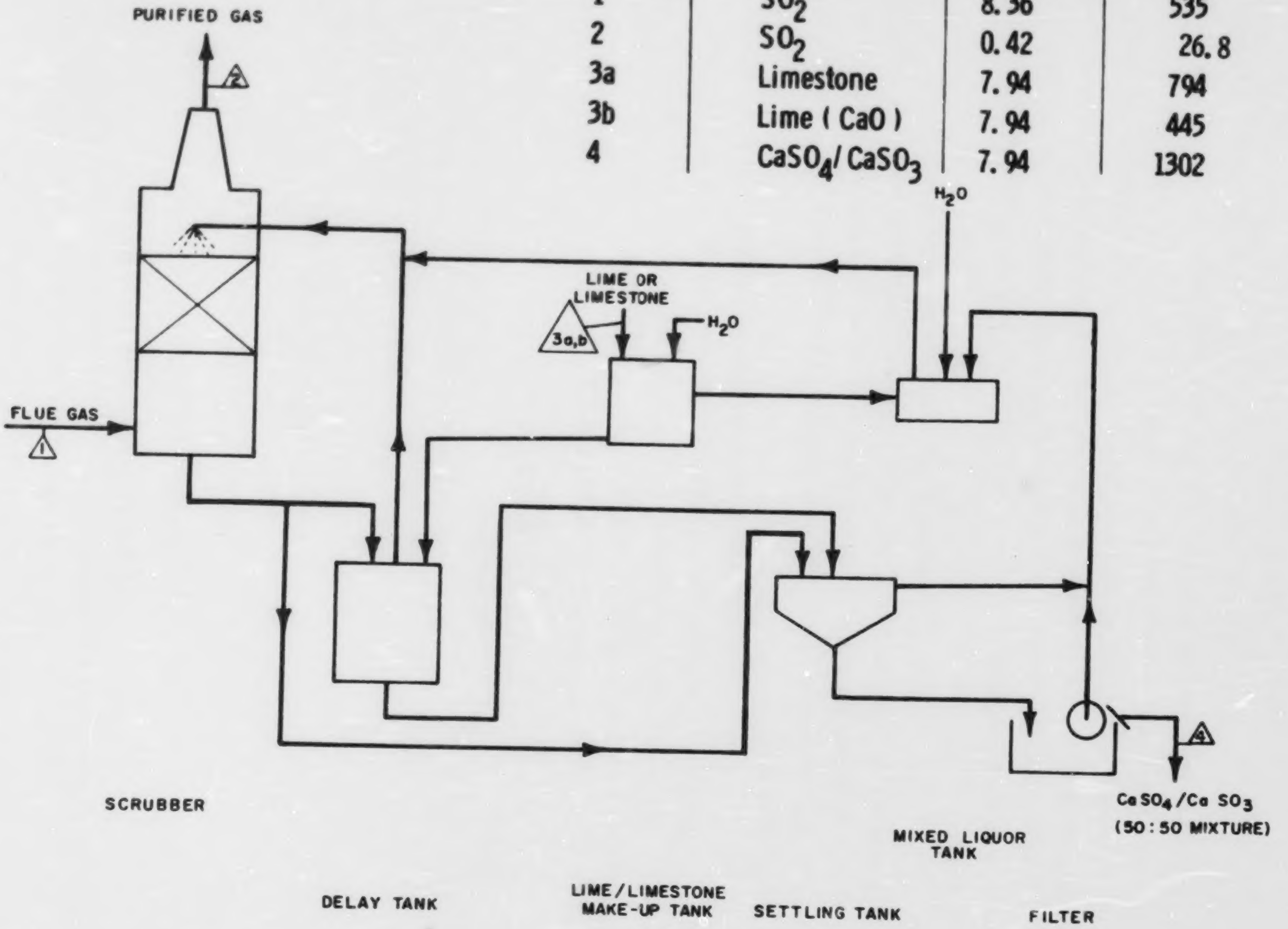
$$CaCO_3\downarrow + H_2O + CO_2 \rightleftharpoons Ca(HCO_3)_2$$

(3) Chemical Requirements and Waste Product Yields

Tables 20 and 21 indicate the raw material requirements and waste-products for treating one million SCF of flue gas by the Howden-I. C. I. process. Table 20 shows the requirements when lime is used as the raw material and Table 21 presents similar data for limestone.

Reactant Chemicals Per Million SCF Flue Gas Processed

Stream	Component	Lb Moles	Lbs
1	SO_2	8.36	535
2	SO_2	0.42	26.8
3a	Limestone	7.94	794
3b	Lime (CaO)	7.94	445
4	$CaSO_4/CaSO_3$	7.94	1302


PURIFIED GAS
2
FLUE GAS
1
H_2O
LIME OR LIMESTONE
3a,b
H_2O
4
$CaSO_4/CaSO_3$
(50 : 50 MIXTURE)
SCRUBBER
DELAY TANK
LIME/LIMESTONE MAKE-UP TANK
SETTLING TANK
MIXED LIQUOR TANK
FILTER

HOWDEN I.C.I. (CYCLIC LIME) AND MITSUBISHI SIMPLIFIED LIME PROCESSES : FLOW DIAGRAM

Figure 12

TABLE 20

HOWDEN-I. C. I. (CYCLIC LIME) PROCESS:

CHEMICAL REQUIREMENTS & BY-PRODUCT YIELDS FOR THE SYSTEM USING LIME

	Quantity per Million SCF Flue Gas		Tons per Year		
	Lb Mole	Lb	20 Million SCFH Flue Gas	0. 5 Million SCFM Flue Gas	2. 5 Million SCFM Flue Gas
Raw Materials					
SO_2 (flue gas)	7. 94	508	40, 230	60, 350	301, 730
CaO	7. 94	445	35, 215	52, 825	264, 115
By-Products					
$CaSO_3/CaSO_4$[a]	7. 94	1302	103, 120	154, 680	773, 390

---

[a] Assumes 50% $SO_3^=$ oxidized to $SO_4^=$.
Values shown based on the hydrated sulfite and sulfate, i. e., $CaSO_3 \cdot 2H_2O$ and $CaSO_4 \cdot 2H_2O$

TABLE 21

HOWDEN-I.C.I. (CYCLIC LIME) PROCESS:

CHEMICAL REQUIREMENTS & BY-PRODUCT YIELDS FOR THE SYSTEM USING LIMESTONE

	Quantity per Million SCF Flue Gas		Tons per Year		
	Lb Mole	Lb	20 Million SCFH Flue Gas	0.5 Million SCFM Flue Gas	2.5 Million SCFM Flue Gas
Raw Materials					
SO_2 (flue gas)	7.94	508	40,230	60,350	301,730
$CaCO_3$[a]	10.72	1128	89,370	134,055	670,340
By-Products					
$CaSO_3/CaSO_4$[b]	7.94	1302	103,120	154,680	773,390

---

[a] Assumes 35% excess of $CaCO_3$ of 95% purity.

[b] Assumes 50% of $SO_3^=$ oxidized to $SO_4^=$.

Values shown based on the hydrated sulfite and sulfate, i.e., $CaSO_3 \cdot 2H_2O$ and $CaSO_4 \cdot 2H_2O$.

As stated in reference 329, the amount of lime required is essentially the stoichiometric amount, whereas a 35% excess of limestone is used. In addition, the referenced report states that 30-80% of the calcium sulfite is oxidized to the sulfate in the process. For purposes of this cost estimate, a 50% oxidation was assumed.

(4) Cost Estimate

Bureau of Mines data[621] were used as the basis for this cost estimate.

(a) Capital Costs

The capital cost estimates in the Bureau of Mines study are reproduced below:

Fixed capital	$1,811,100
Working capital	181,100
Total Investment:	$1,922,200

Up-dating these costs to November 1967 resulted in a total investment of $2,659,700, or $22.16/kw capacity, see Table 22.

(b) Operating Costs

Two operating cost estimates were prepared, depending on whether lime or limestone was used as the raw material. These estimates are presented as Tables 23 and 24, respectively. The costs are as follows:

	Lime	Limestone
Total Operating Cost	$1,996,500	$2,507,200
$/ton of coal	4.20	5.28
mill/kwh	2.10	2.64

The estimates are presented as Tables 23 and 24, respectively. The raw material requirements are as follows:

Plant using lime:	35,215 tons of lime
Plant using limestone*:	89,370 tons of limestone

Direct labor was assumed to be the same as in the Bureau of Mines study, i.e., 4 shifts of 4 men per shift, or 16 men.

---

* A 35% excess of limestone was assumed.

TABLE 22

HOWDEN-I.C.I. (CYCLIC LIME) PROCESS: CAPITAL COST ESTIMATE SUMMARY

	ITEM	FACTOR	COST - $
1.	Purchased Equipment	1.00	510,500
2.	Erection Labor	0.25	127,600
3.	Foundation & Platforms	0.18	91,900
4.	Piping	0.76	388,000
5.	Instruments	0.15	76,600
6.	Insulation	0.08	40,800
7.	Electrical	0.10	51,100
8.	Buildings	0.25	127,600
9.	Land & Yard Improvements	0.13	66,400
10.	Utilities	0.40	204,200
11.	Physical-Plant Cost	3.30	1,684,700
12.	Engineering & Construction	0.66	336,900
13.	Direct Plant Cost	3.96	2,021,600
14.	Contractor's Fee	0.19	97,000
15.	Contingency	0.59	301,200
16.	Fixed Capital Cost	4.74	2,419,800
17.	Working Capital, 10%	0.47	239,900
	Total Investment	5.21	2,659,700

18. Capital Requirements
$/kw capacity 22.16

TABLE 23

HOWDEN-I.C.I. (CYCLIC LIME) PROCESS: OPERATING COST ESTIMATE SUMMARY

(Lime Used @ $15.50/ton)

Fixed Capital Cost: $2,419,800

	ITEM	TOTAL $	%
1.	Raw Materials & Chemicals	545,800	27.34
2.	Direct Labor	96,000	4.81
3.	Supervision	43,200	2.16
4.	Maintenance, 5% of Fixed Capital	121,000	6.06
5.	Supplies, 15% of Maintenance	18,200	0.91
6.	Utilities	56,200	2.82
7.	Other	-	-
8.	TOTAL DIRECT COST	880,400	44.10
9.	Payroll Burden, 20% of 2 & 3	27,800	1.39
10.	Plant Overhead, 50% of 2, 3, 4 & 5	139,200	6.97
11.	Pack & Ship	-	-
12.	Waste Disposal	634,500	31.78
13.	Other	-	-
14.	TOTAL INDIRECT COST	801,500	40.16
15.	Depreciation, 10 % Fixed Capital/Yr	242,000	12.12
16.	Taxes, 2% of Fixed Capital	48,400	2.42
17.	Insurance, 1% of Fixed Capital	24,200	1.21
18.	Other	-	-
19.	TOTAL FIXED COST	314,600	15.76
20.	TOTAL OPERATING COST	1,996,500	100.00
21.	COST: $/Ton of Coal 4.20		
22.	Mill/kwh 2.10		
23.	BY-PRODUCT CREDIT	NOT APPLIED	

TABLE 24

HOWDEN-I. C. I. (CYCLIC LIME) PROCESS: OPERATING COST ESTIMATE SUMMARY

(Limestone Used @ $10/ton)

Fixed Capital Cost: $2,419,800

	ITEM	TOTAL $	%
1.	Raw Materials & Chemicals	893,400	35.63
2.	Direct Labor	96,000	3.83
3.	Supervision	43,200	1.72
4.	Maintenance, 5% of Fixed Capital	121,000	4.83
5.	Supplies, 15% of Maintenance	18,200	0.73
6.	Utilities	56,200	2.24
7.	Other	-	-
8.	TOTAL DIRECT COST	1,228,000	48.98
9.	Payroll Burden, 20% of 2 & 3	27,800	1.11
10.	Plant Overhead, 50% of 2, 3, 4 & 5	139,200	5.55
11.	Pack & Ship	-	-
12.	Waste Disposal	797,600	31.81
13.	Other	-	-
14.	TOTAL INDIRECT COST	964,600	38.47
15.	Depreciation, 10 % Fixed Capital/Yr	242,000	9.65
16.	Taxes, 2% of Fixed Capital	48,400	1.93
17.	Insurance, 1% of Fixed Capital	24,200	0.97
18.	Other	-	-
19.	TOTAL FIXED COST	314,600	12.55
20.	TOTAL OPERATING COST	2,507,200	100.00

21. COST: $/Ton of Coal 5.28
22. Mill/kwh 2.64

23. BY-PRODUCT CREDIT NOT APPLIED

Supervision requirements were assumed as one foreman per shift, and one area superintendent.

The utility requirements were obtained by factoring of the Bureau of Mines estimates, so as to apply to a 95% SO_2 removal rather than the 90% which was considered in the Bureau of Mines work.

Power:	7,817,000 kwh per year
Makeup Water:	93,298,000 gallons per year

For purposes of determining the tonnage of waste materials generated by this system, it was assumed that 50% of the calcium sulfite was oxidized to calcium sulfate. Accordingly, 103,120 tons of calcium sulfite/calcium sulfate are generated for the case where lime is used. It was also assumed that the total weight of the waste would include 35% of free water. Therefore, the total weight of waste became 158,640 tons.

In the case where limestone is used the total weight of waste was 184,000 tons, again on the basis that the cake contained 35% free water.

(c) Process Costs Using Limestone vs Lime

Although this estimate was made using lime and limestone costs of $15.50 and $10.00 per ton, respectively, it is recognized that these figures may vary markedly depending upon availability at any particular plant location. Thus the selection of either raw material will ultimately depend on its delivered cost at the plant.

The use of cost values cited in a recent article[180] would have a very significant affect on process costs. In this paper, in which a dry limestone process was compared with other dry processes, the following unit costs were used:

Limestone:	$2 per ton, delivered
Waste hauling and disposal:	$0.80 per ton, net

These costs, applied to those given in Table 24, would reduce the raw material cost by $714,700 and the waste disposal by $638,100, resulting in a total operating cost of $1,154,400. The unit cost in terms of dollars per ton of coal would thus be reduced from $5.28 to $2.43. There is a large variance in reported limestone costs ($2 to $10/ton) and in disposal costs ($0.80 to $4.00/ton), which probably are influenced by location and availability of the limestone. The $10/ton cost of limestone used in this analysis was quoted from representatives of the United Lime Division of Flintkote Company, Los Angeles. The $4.00 hauling and disposal cost used in the present study was estimated from data given in Reference 57.

(d) Profitability

Since there are no by-products of value produced, credits cannot be applied to this process.

g. Battersea Process

(1) Process Description

In the Battersea process alkaline water is used for scrubbing sulfur dioxide from flue gas. The scrubbing capacity of such a medium is low, and large quantities of water are therefore required. The most suitable water source is an alkaline river, which also serves as an acceptor for the effluent water. Chalk or lime is added to the incoming water in order to increase its alkalinity. The effluent is then treated with manganese sulfate and air so that sulfate, rather than sulfite, can be returned to the river. The oxidation is necessary in order to avoid any subsequent liberation of sulfur dioxide downstream as a result of hydrolysis of the sulfite. A flow diagram of the system is presented in Figure 13.

(2) Process Reactions

Scrubber:

$$SO_2 + CaCO_3 \longrightarrow CaSO_3 \downarrow + CO_2$$

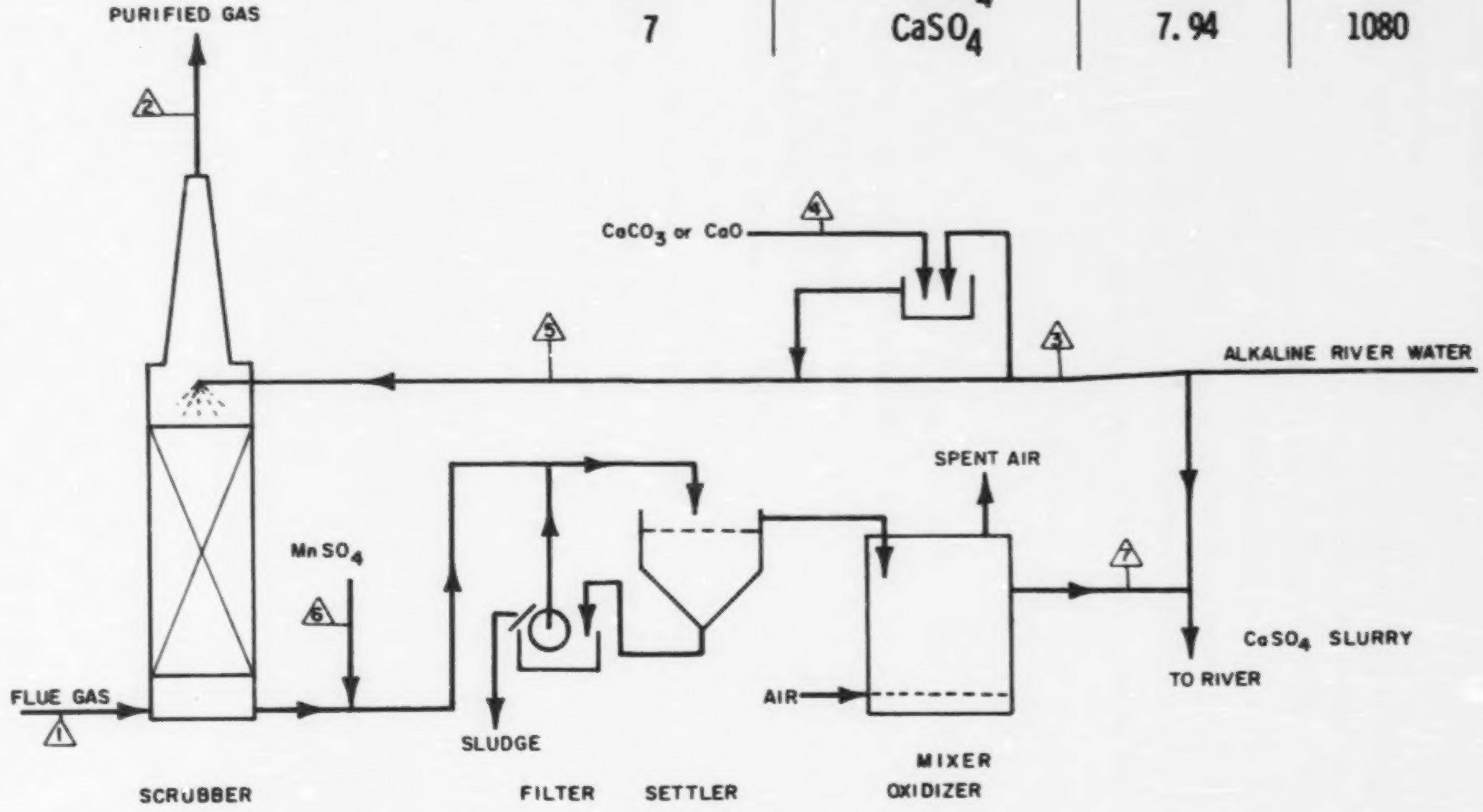
or $$SO_2 + CaO \longrightarrow CaSO_3 \downarrow$$

Oxidizing Tank:

$$CaSO_3 \downarrow + 1/2\ O_2 \longrightarrow CaSO_4 \downarrow$$

Reactant Chemicals Per Million SCF Flue Gas Processed

△ Stream	Component	Lb Moles	Lbs
1	SO_2	8.36	535
2	SO_2	0.42	26.8
3	CaO	6.35	356
4	CaO	1.59	89
5	CaO	7.94	445
6	$MnSO_4$	0.018	2.7
7	$CaSO_4$	7.94	1080


PURIFIED GAS
2
CaCO₃ or CaO
4
5
3
ALKALINE RIVER WATER
SPENT AIR
MnSO₄
6
7
CaSO₄ SLURRY
TO RIVER
FLUE GAS
1
AIR
SLUDGE
SCRUBBER
FILTER
SETTLER
MIXER
OXIDIZER

BATTERSEA PROCESS : FLOW DIAGRAM

Figure 13

(3) Chemical Requirements and By-Product Yields

Table 25 lists the raw material requirements and by-product (waste) yields for treating one million SCF of flue gas by the Battersea process. The SO_2, calcium oxide and calcium sulfate quantities are based on stoichiometric values. The water and manganese sulfate requirements are based on the data reported by Rees;[357] the manganese sulfate requirement was, in fact, increased in the present study in proportion to the greater SO_2 content (0. 3%) of the standard flue gas as compared to that treated in the Battersea plant. The waste mud quantities were also taken from this reference.

(4) Cost Estimate

The Battersea process is an effluent system in that the scrubbing medium is used on a once-through basis and is discharged into a waterway. Since the large quantities of water required limit its applicability to select locations where water availability permits a noneffluent system, the Howden-I. C. I. (Cyclic Lime) process was subsequently developed. (A detailed discussion of the latter process is presented in the preceding section of this report). Because of the fact that the two processes are similar and were both developed by the English, the two have been compared to some extent on an economic basis. Accordingly, cost-estimate data for the Howden-I. C. I. process was applied to the Battersea process when applicable.

(a) Capital Costs

Literature data[108] indicate that the capital investment for a plant which incorporates the Battersea process is approximately two-thirds as great as the cost of a comparable sized plant which employs the Howden - I. C. I. process. The purchased equipment cost of the Howden - I. C. I. process was estimated at $510, 500 (Table 22). The purchased equipment cost for the Battersea process is therefore $340, 500. Table 26 summarizes the capital costs. The total investment is $1, 774, 100, or $14. 78/kw capacity.

TABLE 25

BATTERSEA PROCESS:
CHEMICAL REQUIREMENTS & BY-PRODUCT YIELDS

	Quantity per Million SCF Flue Gas		Tons per Year		
	Lb Mole	Lb	20 Million SCFH Flue Gas	0.5 Million SCFM Flue Gas	2.5 Million SCFM Flue Gas
Raw Materials					
SO_2 (flue gas)	7.94	508	40,230	60,350	301,730
H_2O Containing 200 ppm CaO					
CaO (80% theor.)	6.35	356	28,200	42,300	211,500
H_2O	10,890	196,000	15,523,200 (7830)[a]	23,284,800 (11,750)[a]	116,424,000 (58,750)[a]
$CaCO_3$ (20% theor.)	1.59	159	12,590	18,885	94,425
$MnSO_4$	0.06	9	713	1,070	5,350
By-Products					
Mud (wet solid waste)	-	45	3,565	5,345	26,730
$CaSO_4$[b] (in effluent water)	7.94	1080	85,540	128,310	641,550

---

[a] Equivalent Water Rate, gpm

[b] Values shown based on hydrated sulfate, i.e., $CaSO_4 \cdot 2H_2O$

TABLE 26

BATTERSEA PROCESS: CAPITAL COST ESTIMATE SUMMARY

	ITEM	FACTOR	COST - $
1.	Purchased Equipment	1.00	340,500
2.	Erection Labor	0.25	85,100
3.	Foundation & Platforms	0.18	61,300
4.	Piping	0.76	258,800
5.	Instruments	0.15	51,100
6.	Insulation	0.08	27,200
7.	Electrical	0.10	34,100
8.	Buildings	0.25	85,100
9.	Land & Yard Improvements	0.13	44,300
10.	Utilities	0.40	136,200
11.	Physical-Plant Cost	3.30	1,123,700
12.	Engineering & Construction	0.66	224,700
13.	Direct Plant Cost	3.96	1,348,400
14.	Contractor's Fee	0.19	64,700
15.	Contingency	0.59	200,900
16.	Fixed Capital Cost	4.74	1,614,000
17.	Working Capital, 10%	0.47	160,100
	Total Investment	5.21	1,774,100

18. Capital Requirements
$/kw capacity 14.78

(b) Operating Costs

Two operating-cost summaries were prepared. Table 27 illustrates a case in which alkaline water, similar to the Thames Water, is used. The alkalinity of this water provides 80% of the reactant for the SO_2 in the flue gas. The remaining 20% reactant is provided in the form of limestone. Table 28 lists the cost when chemically neutral water is used and all of the limestone is added as slurry. The costs are as follows:

	Thames Water	Neutral Water
Total Operating Cost	$851,000	$1,383,000
$/ton of coal	1.80	2.92
mill/kwh	0.90	1.46

Both direct labor and supervision were considered to be the same as in the Howden-I. C. I. process, i. e., 4 operators and 1 foreman per shift and one area superintendent.

The utilities cost in this system is less than in the Howden-I. C. I. process because it was assumed that water would be available at no cost other than pumping charges which were included in the power cost.

A relatively small charge for waste disposal was included to handle the "mud" removed from the system.

Reference to operating cost, in terms of dollars per ton of coal and mills per kwh, indicates a relatively inexpensive system for SO_2 removal from flue gas, especially when using alkaline water.

(c) Profitability

Since there are no by-products of value to recover, credits cannot be applied to this process.

TABLE 27

BATTERSEA PROCESS: OPERATING COST ESTIMATE SUMMARY
(Thames River Water)

Fixed Capital Cost: $1,614,000

	ITEM		TOTAL $	%
1.	Raw Materials & Chemicals		204,300	24.01
2.	Direct Labor		96,000	11.28
3.	Supervision		43,200	5.08
4.	Maintenance, 5% of Fixed Capital		80,700	9.48
5.	Supplies, 15% of Maintenance		12,100	1.42
6.	Utilities		46,900	5.51
7.	Other		-	-
8.	TOTAL DIRECT COST		483,200	56.78
9.	Payroll Burden, 20% of 2 & 3		27,800	3.27
10.	Plant Overhead, 50% of 2, 3, 4 & 5		116,000	13.63
11.	Pack & Ship		-	-
12.	Waste Disposal		14,200	1.67
13.	Other		-	-
14.	TOTAL INDIRECT COST		158,000	18.57
15.	Depreciation, 10 % Fixed Capital/Yr		161,400	18.96
16.	Taxes, 2% of Fixed Capital		32,300	3.80
17.	Insurance, 1% of Fixed Capital		16,100	1.89
18.	Other		-	-
19.	TOTAL FIXED COST		209,800	24.65
20.	TOTAL OPERATING COST		851,000	100.00
21.	COST: $/Ton of Coal	1.80		
22.	Mill/kwh	0.90		
23.	BY-PRODUCT CREDIT		NOT APPLIED	

TABLE 28

BATTERSEA PROCESS: OPERATING COST ESTIMATE SUMMARY
(Neutral Water)

Fixed Capital Cost: $1,614,000

	ITEM	TOTAL $	%
1.	Raw Materials & Chemicals	736,300	53.24
2.	Direct Labor	96,000	6.94
3.	Supervision	43,200	3.12
4.	Maintenance, 5% of Fixed Capital	80,700	5.84
5.	Supplies, 15% of Maintenance	12,100	0.88
6.	Utilities	46,900	3.39
7.	Other	-	-
8.	TOTAL DIRECT COST	1,015,200	73.41
9.	Payroll Burden, 20% of 2 & 3	27,800	2.01
10.	Plant Overhead, 50% of 2, 3, 4 & 5	116,000	8.39
11.	Pack & Ship	-	-
12.	Waste Disposal	14,200	1.02
13.	Other	-	-
14.	TOTAL INDIRECT COST	158,000	11.42
15.	Depreciation, 10 % Fixed Capital/Yr	161,400	11.67
16.	Taxes, 2% of Fixed Capital	32,300	2.34
17.	Insurance, 1% of Fixed Capital	16,100	1.16
18.	Other	-	-
19.	TOTAL FIXED COST	209,800	15.17
20.	TOTAL OPERATING COST	1,383,000	100.00

21. COST: $/Ton of Coal 2.92
22. Mill/kwh 1.46

23. BY-PRODUCT CREDIT NOT APPLIED

h. Magnesium Hydroxide Process

(1) Process Description

In the Magnesium Hydroxide process, the SO_2 is scrubbed from the flue gas by reacting it with a slurry of magnesium hydroxide.[541] The scrubber liquid which contains magnesium sulfite formed in the reaction is aerated to oxidize the sulfite to sulfate. Synthetic ammonia is then added to the circulating medium to regenerate the magnesium hydroxide.

A portion of the circulating medium is continuously drawn off for product recovery. This side stream is filtered to remove the solid magnesium hydroxide contained therein, vacuum evaporated, centrifuged, and dried to recover the product ammonium sulfate. The magnesium hydroxide precipitate from this side stream is returned to the circulating medium. A flow diagram of the process is presented in Figure 14.

(2) Process Reactions

SO_2 Scrubber:

$$Mg(OH)_2 \downarrow + SO_2 \longrightarrow MgSO_3 \downarrow + H_2O$$

Oxidizer:

$$MgSO_3 \downarrow + 1/2\ O_2 \longrightarrow MgSO_4$$

Mixer:

$$MgSO_4 + 2H_2O + 2NH_3 \longrightarrow Mg(OH)_2 \downarrow + (NH_4)_2SO_4$$

(3) Chemical Requirements and By-Product Yields

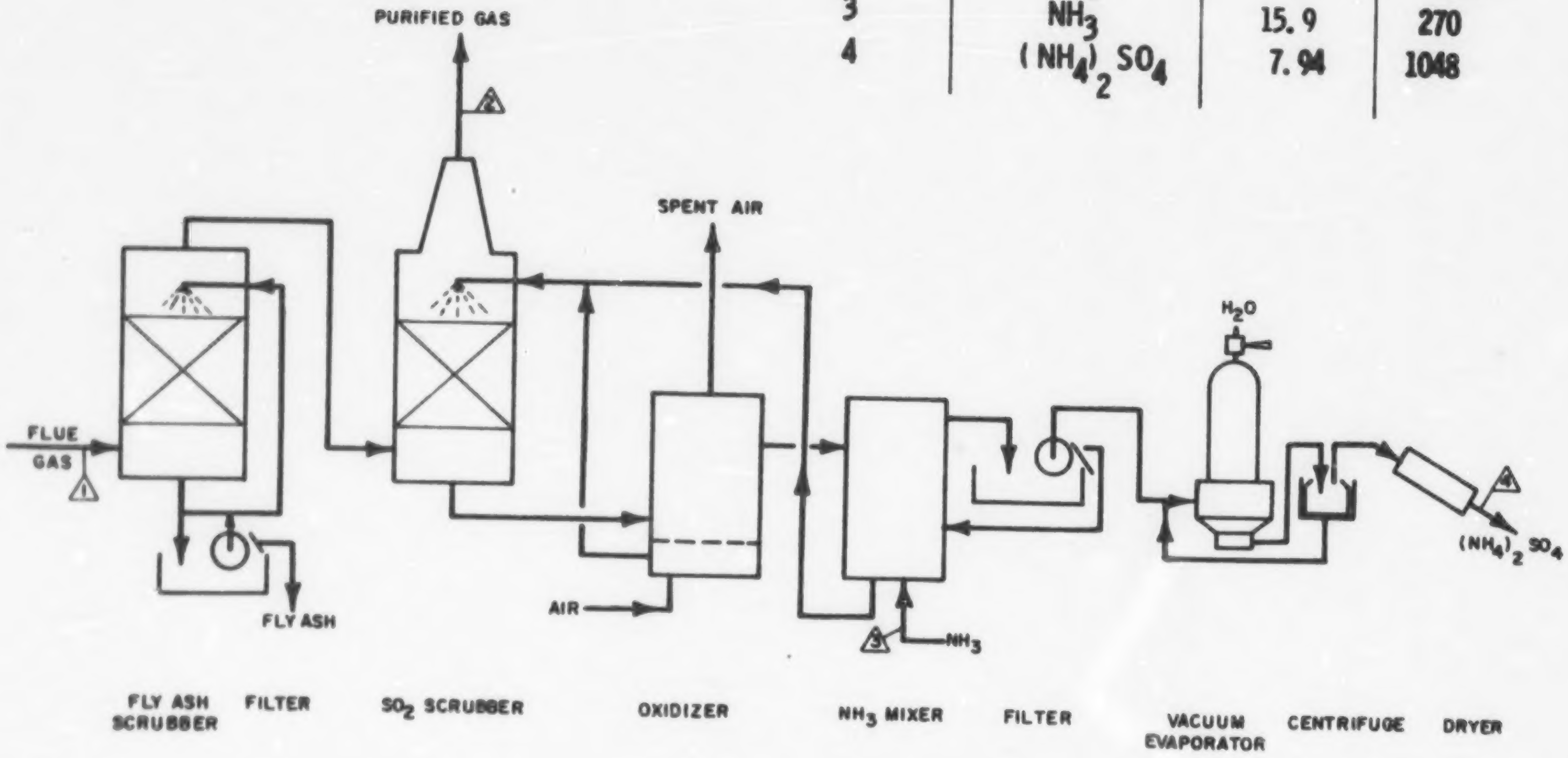
Table 29 gives the chemical requirements and by-product yields per million SCF of flue gas processed. Ammonia is the only chemical requirement needed and ammonium sulfate is the only by-product.

(4) Fly-Ash Removal

The Magnesium Hydroxide process presented a special problem as the result of the requirement for removing the fly ash entrained in the flue gas. The problem was not a common one for the systems studied up to

Reactant Chemicals Per Million SCF Flue Gas Processed

△ Stream	Component	Lb Moles	Lbs
1	SO_2	8.36	535
2	SO_2	0.42	26.8
3	NH_3	15.9	270
4	$(NH_4)_2SO_4$	7.94	1048


PURIFIED GAS
2
SPENT AIR
FLUE GAS
1
FLY ASH
AIR
3
NH3
H2O
4
(NH4)2 SO4
FLY ASH SCRUBBER
FILTER
SO2 SCRUBBER
OXIDIZER
NH3 MIXER
FILTER
VACUUM EVAPORATOR
CENTRIFUGE
DRYER

MAGNESIUM HYDROXIDE PROCESS: FLOW DIAGRAM

Figure 14

TABLE 29

MAGNESIUM HYDROXIDE PROCESS: CHEMICAL REQUIREMENTS & BY-PRODUCT YIELDS

	Quantity per Million SCF Flue Gas		Tons per Year		
	Lb Mole	Lb	20 Million SCFH Flue Gas	0.5 Million SCFM Flue Gas	2.5 Million SCFM Flue Gas
Raw Materials					
SO_2 (flue gas)	7.94	508	40,230	60,350	301,730
NH_3 (anhyd.)	15.88	270	21,380	32,070	160,350
By-Product					
$(NH_4)_2SO_4$	7.94	1048	83,000	124,500	622,500

this point because fly ash constituted the only particulate matter in the scrubbing solutions and was easily removed by a simple filtration step. In this instance, however, the scrubbing solution contains particulate magnesium sulfite and magnesium hydroxide which cannot be discarded without introducing high additional costs to the process.

One method which can be used to circumvent the problem cited above is to acidify a portion of the circulating medium with sulfuric acid to render the magnesium soluble, filter off the fly ash, and neutralize with additional ammonia to recover the magnesium as magnesium hydroxide. Another method involves incorporation of a fly ash scrubber similar in construction to the SO_2 scrubber with the exception that only water would be circulated. The fly ash would be removed by filtration of this circulating water.

Preliminary cost considerations indicated that removal by filtration of the magnesium sulfite and magnesium hydroxide together with the fly ash would increase the annual operating costs for the process by about $11,000,000. The sulfuric acid approach would increase the cost by approximately $6,000,000. On the other hand, it was estimated that annual operating costs for the preliminary fly ash scrubber would be increased by about $300,000, a relatively low cost. Clearly, the first two approaches mentioned may be immediately rejected on the basis of the prohibitively high costs. Accordingly, the fly ash scrubber was selected as the best method to achieve fly ash removal, and it was incorporated in this cost estimate.

(5) Cost Estimate

Other than for the general description of the process given in Reference 541, there was no data available regarding this process. However, the system exhibited similarities to various phases of the Howden-I. C. I., Fulham-Simon-Carves, and Zinc Oxide processes. Hence, the portions of these three well-documented processes which are regarded as applicable to the requirements of the Magnesium Hydroxide process were used as the basis for this cost estimate.

(a) Capital Costs

The fly-ash scrubber is the same as one of the scrubbers used in the Fulham-Simon-Carves system. Choice of the latter was based on the fact that the acidic conditions which would exist in the fly ash scrubber as the result of SO_2 solubility would present no problem in the lead-lined system. A rotary vacuum filter required for the removal of the fly ash from the system is incorporated in this subsystem. Cost: $273,400.

The Howden-I. C. I. system entails the use of a lime or chalk slurry for removing SO_2 from the flue gases. Because of the similarity in the scrubbing medium in the Howden-I. C. I. process and the Magnesium Hydroxide process, the scrubber assembly used for the former was considered to be suitable for the latter process. Cost: $263,600.

The air oxidation and mixer subsystems were based on the use of two 150,000 gal tanks of lead-lined steel construction. An air compressor completes this system. Cost: $93,400.

The product recovery subsystem in the Fulham-Simon-Carves process, with the exception of the autoclaves, was applied to this process. Cost: $428,900.

Storage facilities were estimated to cost $301,000.

Miscellaneous pumps resulted in an additional cost of $32,000.

The total purchased equipment cost amounted to $1,392,300. The total capital investment of $7,253,900, or $60.53/kw capacity is summarized in Table 30.

(b) Operating Costs

The chemical requirements for the Magnesium Hydroxide process are listed in Table 29. It is worthy of note that anhydrous ammonia is the only raw material requirement and ammonium sulfate is the only salable by-product.

TABLE 30

MAGNESIUM HYDROXIDE PROCESS: CAPITAL COST ESTIMATE SUMMARY

	ITEM	FACTOR	COST - $
1.	Purchased Equipment	1.00	1,392,300
2.	Erection Labor	0.25	348,100
3.	Foundation & Platforms	0.18	250,600
4.	Piping	0.76	1,058,100
5.	Instruments	0.15	208,800
6.	Insulation	0.08	111,400
7.	Electrical	0.10	139,200
8.	Buildings	0.25	348,100
9.	Land & Yard Improvements	0.13	181,000
10.	Utilities	0.40	556,900
11.	Physical-Plant Cost	3.30	4,594,600
12.	Engineering & Construction	0.66	918,900
13.	Direct Plant Cost	3.96	5,513,500
14.	Contractor's Fee	0.19	264,500
15.	Contingency	0.59	821,500
16.	Fixed Capital Cost	4.74	6,599,500
17.	Working Capital, 10%	0.47	654,400
	Total Investment	5.21	7,253,900

18. Capital Requirements
$/kw capacity 60.45

The estimated annual operating cost is $3,260,100, or $6.86/ton of coal and 3.43 mill/kwh. See Table 31. The cost for anhydrous ammonia was assumed to be $60 per ton.

Direct labor was assumed to be the same as for the Fulham-Simon-Carves process in the Bureau of Mines study. Supervision was assumed as one foreman per shift, and one area superintendent.

The utilities requirements for the Magnesium Hydroxide process were based upon the data presented in the Bureau of Mines report. A listing follows:

Steam:	229,000 M lb per year
Power:	10,807,000 kwh per year
Make-up Water:	200,000 M gal per year
Circulating Water:	975,000 M gal per year

(c) Profitability

Figure 15 indicates the profitability for the Magnesium Hydroxide system, or a probable net cost of approximately $4-4.50/ton of coal and 2-2.25 mill/kwh.

i. Magnesium Oxide Process

(1) Process Description

In the Magnesium Oxide process, the sulfur dioxide is scrubbed from the flue gas by reacting it with a slurry containing excess magnesium sulfite.[598] The magnesium bisulfite obtained from this reaction is then neutralized with magnesium oxide to regenerate the magnesium sulfite, which is returned to the scrubber.

A portion of the regenerated magnesium sulfite slurry is continuously drawn off for product recovery. The insoluble magnesium sulfite is filtered, dried and calcined, resulting in by-product sulfur dioxide and magnesium oxide, which is reused in the neutralization step.

As in the Zinc Oxide process, a complication arises as the result of the partial oxidation of the sulfite to sulfate in both the calciner

TABLE 31

MAGNESIUM HYDROXIDE PROCESS: OPERATING COST ESTIMATE SUMMARY

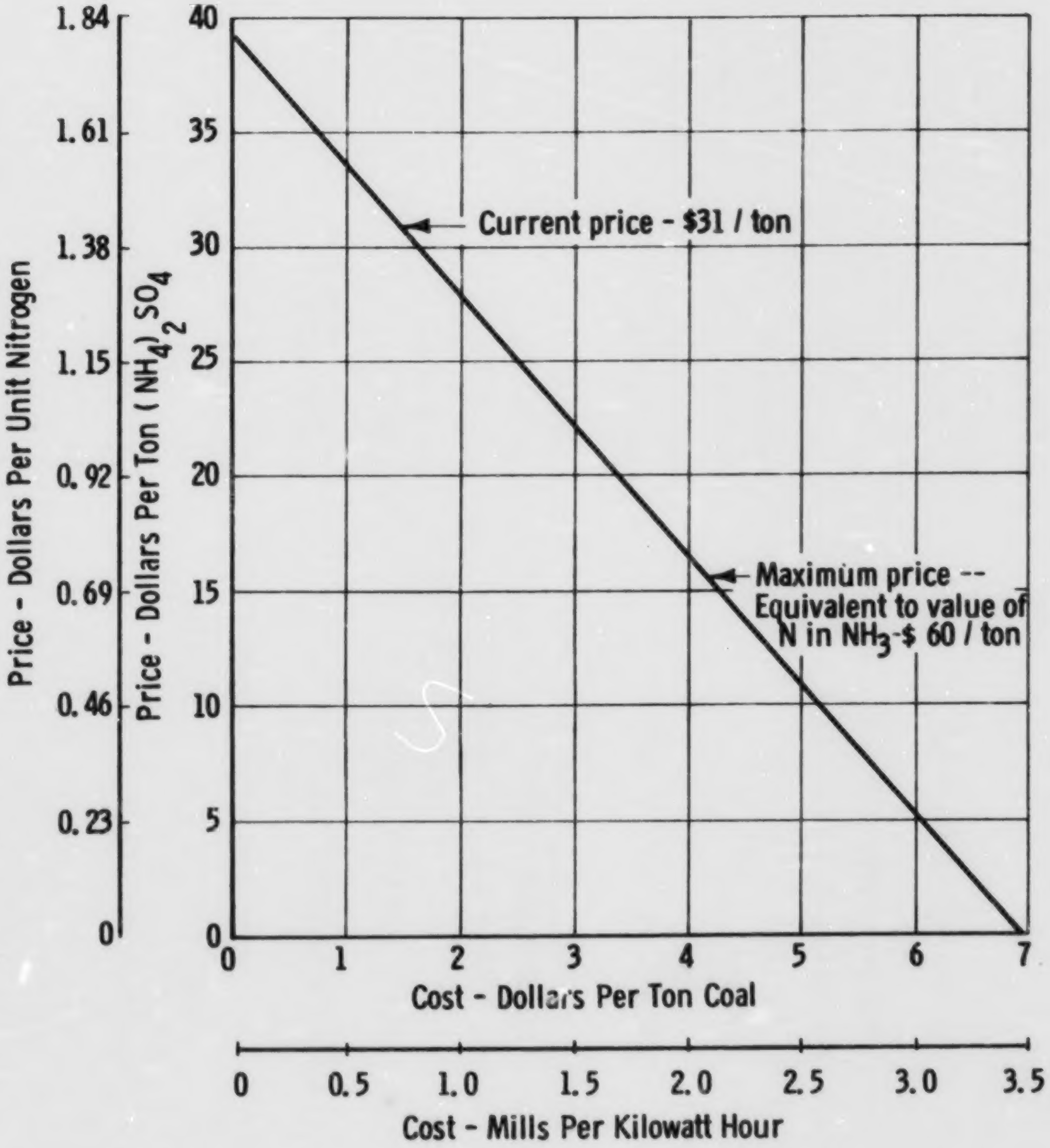
Fixed Capital Cost: $6,599,500

	ITEM	TOTAL $	%
1.	Raw Materials & Chemicals	1,282,800	39.35
2.	Direct Labor	120,000	3.68
3.	Supervision	43,200	1.33
4.	Maintenance, 5% of Fixed Capital	330,000	10.12
5.	Supplies, 15% of Maintenance	49,500	1.52
6.	Utilities	272,600	8.36
7.	Other	-	-
8.	TOTAL DIRECT COST	2,098,100	64.36
9.	Payroll Burden, 20% of 2 & 3	32,600	1.00
10.	Plant Overhead, 50% of 2, 3, 4 & 5	271,400	8.32
11.	Pack & Ship	-	-
12.	Waste Disposal	-	-
13.	Other	-	-
14.	TOTAL INDIRECT COST	304,000	9.32
15.	Depreciation, 10 % Fixed Capital/Yr	660,000	20.24
16.	Taxes, 2% of Fixed Capital	132,000	4.05
17.	Insurance, 1% of Fixed Capital	66,000	2.02
18.	Other	-	-
19.	TOTAL FIXED COST	858,000	26.32
20.	TOTAL OPERATING COST	3,260,100	100.00

21. COST: $/Ton of Coal 6.86

22. Mill/kwh 3.43

23. BY-PRODUCT CREDIT (SEE FIGURE 15)



Basis :
- 120 megawatt power plant
- 20 million cfh flue gas
- Sale of 83,000 tons $(NH_4)_2SO_4$ per year

MAGNESIUM HYDROXIDE PROCESS : PROFITABILITY

Figure 15

and scrubber sections of the system. To prevent an excessive buildup of sulfate, the filtrate from the magnesium sulfite filtration is diverted to an evaporating pond, from which magnesium sulfate is ultimately removed for disposal. Johnstone and Singh[594] indicate that approximately 10% of the absorbed sulfur dioxide is oxidized in the scrubber. In addition, these workers estimated that 20% of the calcined magnesium sulfite would also undergo oxidation in the calciner. Accordingly, it was assumed in the preparation of this cost estimate that 28% of the absorbed sulfur dioxide will undergo oxidation. Recent developments, by others, suggest that the degree of SO_2 oxidation can be considerably less than the value assumed herein; the effect of oxidation on process economics is quite substantial.

A further process complication exists because of the waste materials contained in the 95% pure magnesium oxide raw material. Discussion with representatives of the Inorganic Chemicals Division of FMC Corporation indicated that these waste materials consist of the oxides of calcium, silicon, iron, and boron. These materials are expected to be insoluble in basic media and would tend to build up in the system. Accordingly, these wastes are removed from the system by discarding a portion of the precipitate from the magnesium sulfite filtration. For the purpose of this cost estimate, it was assumed that 5% of the precipitate is discarded. Fly ash is removed in a prescrubber so that it does not recycle and build up in the magnesium oxide slurry system. A flow diagram of the process is shown in Figure 16.

(2) Process Reactions

Scrubber:

$$MgSO_3 \downarrow + SO_2 + H_2O \longrightarrow Mg(HSO_3)_2$$

$$MgSO_3 \downarrow + 1/2\ O_2 \longrightarrow MgSO_4$$

Neutralization Tank:

$$Mg(HSO_3)_2 + MgO \longrightarrow 2\ MgSO_3 \downarrow + H_2O$$

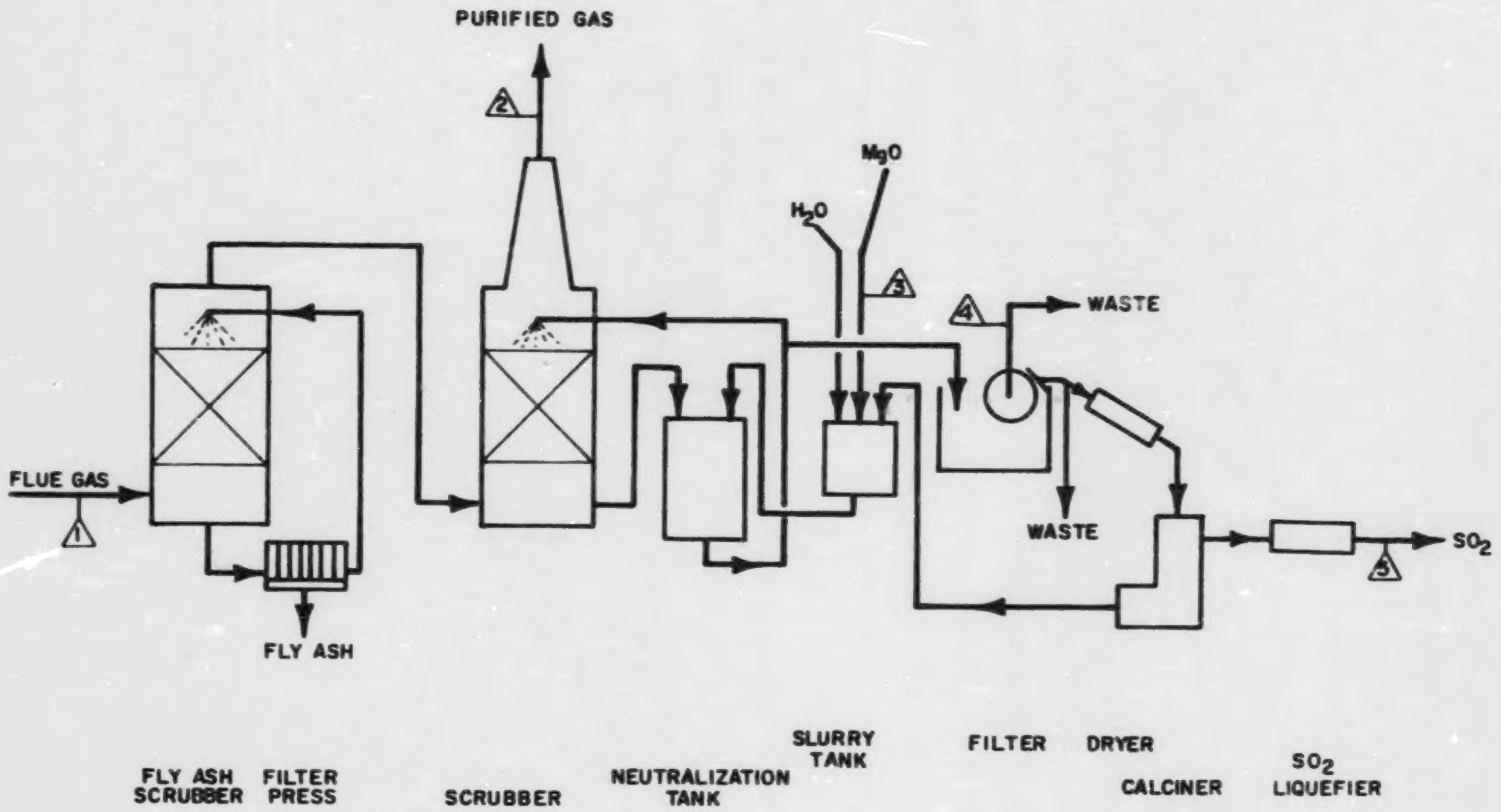
Calciner:

$$MgSO_3 \xrightarrow{\Delta} MgO + SO_2 \text{ (80\% of calcined } MgSO_3\text{)}$$

$$MgSO_3 + 1/2\ O_2 \longrightarrow MgSO_4 \text{ (20\% of calcined } MgSO_3\text{)}$$

Reactant Chemicals Per Million SCF Flue Gas Processed

△ Stream	Component	Lb Moles	Lbs
1	SO_2	8.36	535
2	SO_2	0.42	26.9
3	MgO	2.58	104
4	$MgSO_4$	2.22	267
5	SO_2	5.36	343


PURIFIED GAS
2
MgO
H₂O
3
4
WASTE
FLUE GAS
1
WASTE
SO₂
5
FLY ASH
FLY ASH SCRUBBER
FILTER PRESS
SCRUBBER
NEUTRALIZATION TANK
SLURRY TANK
FILTER
DRYER
CALCINER
SO₂ LIQUEFIER

MAGNESIUM OXIDE PROCESS : FLOW DIAGRAM

Figure 16

(3) Chemical Requirements and By-Product Yields

Table 32 indicates the chemical requirements and by-product yields in treating one million SCF of flue gas by the Magnesium Oxide process.

(4) Cost Estimate

The pulp and paper industry is currently using a regenerative Magnesium Oxide process for pulp manufacture which is similar in principle to the systems designed for removing SO_2 from flue gases. However, the information[598] reported in the literature is qualitative in nature and is of very limited use as far as providing any basis for the present economic study is concerned. One reference indicates that the process has been used in Russia for the recovery of SO_2 from flue gases on a pilot-plant scale. However, no data regarding the results were available.

Because of the similarities of the Magnesium Oxide process with the processes investigated by Field, et al., in the Bureau of Mines study,[621] the latter were used, wherever possible, as the basis of this estimate.

(a) Capital Costs

The same fly-ash scrubber subsystem would be used for the Magnesium Oxide process that was used for the Magnesium Hydroxide process. Cost: $273,400.

The same type of SO_2 scrubber incorporated in the Magnesium Hydroxide process was considered to be adequate for the Magnesium Oxide system. Cost: $263,600.

A 150,000-gal tank was used in the Howden-I.C.I. process[621] to achieve a 3.75-min. time delay. This tank size and delay time is considered adequate to allow neutralization of the magnesium bisulfite obtained as a product in the scrubber reaction. The material of construction is lead-lined steel. Cost: $45,700.

The waste filter having 200 square feet of surface area was estimated to cost $16,000.

TABLE 32

MAGNESIUM OXIDE PROCESS:

CHEMICAL REQUIREMENTS AND BY-PRODUCT YIELDS

	Quantity per Million SCF Flue Gas		Tons per Year		
	Lb Mole	Lb	20 Million SCFH Flue Gas	0.5 Million SCFM Flue Gas	2.5 Million SCFM Flue Gas
Raw Materials					
SO_2 (flue gas)	7.94	508	40,230	60,350	301,730
MgO	2.58	104	8,670	13,005	65,025
By-Products					
$MgSO_4$	2.22	267	21,146	31,720	158,600
SO_2	5.36	343	27,165	40,748	203,737

A comparison of the material handling requirements of the dryer and calciner sections of the Zinc Oxide system cited in the Bureau of Mines report and the Magnesium Oxide process indicates that, with the exception of the calciner operation, the requirements are identical. Accordingly, the costs taken from the Zinc Oxide process study for these items were used in the preparation of this estimate. The following items of equipment were considered to be necessary: dryer, hammer mill, cyclone separators, and blower at a total purchase cost of $79, 200.

The calciner for the Magnesium Oxide process would be used under markedly different operating conditions than that used in the Zinc Oxide system. Effective calcination of zinc sulfite can be achieved by heating the solid to approximately 850°F, whereas calcination of magnesium sulfite requires that the solid be heated to approximately 1200°F. It was considered that the calciner for the magnesium oxide would probably be twice the cost of the unit used in the Zinc Oxide process. Cost: $248, 900.

The cost of the SO_2 liquefaction system was $107, 500. The cost of the slurry tank was estimated at $22, 200.

Various small pieces of equipment would be required including pumps to handle the slurries and solutions, screw conveyors to handle the solids, and the magnesium oxide and magnesium sulfate storage systems. Based on the Bureau of Mines study, a cost of $117, 500 was considered as adequate to cover these items.

From the estimated costs presented in the foregoing, the total purchase price was determined to be $1, 174, 000. The total investment was $6, 116, 600 or $50. 97 per kilowatt capacity. A capital cost summary for the system is given in Table 33.

(b) Operating Costs

The annual requirement for magnesium oxide is listed in Table 32 as 8, 670 tons. The OPD Reporter (5 February 1968) cites a price for calcined 95% magnesium oxide of $61. 00 per ton. Accordingly, the annual cost of raw materials was determined to be $528, 900.

TABLE 33

MAGNESIUM OXIDE PROCESS: CAPITAL COST ESTIMATE SUMMARY

	ITEM	FACTOR	COST - $
1.	Purchased Equipment	1.00	1,174,000
2.	Erection Labor	0.25	293,500
3.	Foundation & Platforms	0.18	211,300
4.	Piping	0.76	892,200
5.	Instruments	0.15	176,100
6.	Insulation	0.08	93,900
7.	Electrical	0.10	117,400
8.	Buildings	0.25	293,500
9.	Land & Yard Improvements	0.13	152,600
10.	Utilities	0.40	469,600
11.	Physical-Plant Cost	3.30	3,874,100
12.	Engineering & Construction	0.66	774,800
13.	Direct Plant Cost	3.96	4,648,900
14.	Contractor's Fee	0.19	223,100
15.	Contingency	0.59	692,700
16.	Fixed Capital Cost	4.74	5,564,700
17.	Working Capital, 10%	0.47	551,800
	Total Investment	5.21	6,116,500

18. Capital Requirements
$/kw capacity 50.97

The annual direct labor and supervision was assumed to be the same as for the Magnesium Hydroxide process.

In the Bureau of Mines study, the utility requirements are presented in itemized form for each of the three systems considered. The present cost estimate for the Magnesium Oxide process was largely based on equipment cited from this earlier study. A listing of utility requirements follows. The requirement for fuel oil was obtained from preliminary claculations of the heat requirements for calcining the magnesium sulfite.

Power:	12,107,000 kwh per year
Steam:	228,000 M lb per year
Make-up Water:	200,000 M gal per year
Circulating Water:	235,000 M gal per year
Fuel Oil:	4,472,000 gal per year

The annual waste disposal cost was based on the assumption that magnesium sulfate heptahydrate and 5% of the solids collected in the magnesium sulfite filtration system would be discarded. Of the total waste, impurities in the magnesium oxid[illegible]mount to 434 tons. The remaining waste, consisting of 6,019 tons of magnesium sulfite hexahydrate and 43,306 tons of magnesium sulfate heptahydrate, would contain excess water. Assuming 35% of the total weight of this waste is water, the total overall waste amounts to 76,550 tons. At $4.00 per ton this became $306,200.

A summary of the total operating costs is presented in Table 34. This annual cost was estimated to be $2,981,500, or $6.27/ton of coal and 3.14 mill/kwh.

(c) Profitability

The OPD Reporter lists the current price of magnesium sulfate as $2.45 per 100 lbs. However, it is doubtful whether large tonnages of this material could be sold at any price. From the meager data available regarding price history, annual consumption, etc., it appeared unjustified at the present time to assume a credit for this material. An independent study was made, however, in which the cost of isolation of magnesium

TABLE 34

MAGNESIUM OXIDE PROCESS: OPERATING COST ESTIMATE SUMMARY

Fixed Capital Cost: $5,564,700

	ITEM	TOTAL $	%
1.	Raw Materials & Chemicals	528,900	17.74
2.	Direct Labor	120,000	4.02
3.	Supervision	43,200	1.45
4.	Maintenance, 5% of Fixed Capital	278,200	9.33
5.	Supplies, 15% of Maintenance	41,700	1.40
6.	Utilities	665,700	22.33
7.	Other	-	-
8.	TOTAL DIRECT COST	1,677,700	56.28
9.	Payroll Burden, 20% of 2 & 3	32,600	1.09
10.	Plant Overhead, 50% of 2, 3, 4 & 5	241,600	8.13
11.	Pack & Ship	-	-
12.	Waste Disposal	306,200	10.27
13.	Other	-	-
14.	TOTAL INDIRECT COST	580,400	19.46
15.	Depreciation, 10 % Fixed Capital/Yr	556,500	18.67
16.	Taxes, 2% of Fixed Capital	111,300	3.73
17.	Insurance, 1% of Fixed Capital	55,600	1.86
18.	Other	-	-
19.	TOTAL FIXED COST	723,400	24.26
20.	TOTAL OPERATING COST	2,981,500	100.00

21. COST: $/Ton of Coal 6.27

22. Mill/kwh 3.14

23. BY-PRODUCT CREDIT (SEE FIGURE 17)

sulfate, via solvent removal, centrifugation, and drying, was determined as an annual operating cost of \$73,700. On this basis the break-even point was determined as \$0.17/100 lbs; therefore, a process credit could be applied if the material could be sold at a price higher than this.

The profitability of the Magnesium Oxide process, based on the annual sale of 27,165 tons of sulfur dioxide, and with no credit applied for magnesium sulfate, is shown in Figure 17. This indicates a net cost of approximately \$5/ton of coal with liquid SO_2 being sold at \$20/ton.

j. Manganese Oxide Process

(1) Process Description

In the Manganese Oxide process, the sulfur dioxide reacts with an aqueous suspension of manganese dioxide to form a solution of manganese sulfate. Manganese dithionate and sulfuric acid are also formed because of the presence of oxygen in the flue gas. A portion of the absorbing solution is continually withdrawn and allowed to settle. The clarified portion is then heated in an autoclave to precipitate the manganese sulfate which is separated, dried, and calcined; the solid manganese oxide is then added to the slurry from the clarifier and the mixture returned to the scrubber. The sulfur dioxide which is released during the calcining step contains about 10% of sulfur trioxide which is separated by liquefaction, converted to a sulfuric acid mist and discharged as waste. A flow diagram of the process is shown in Figure 18.

(2) Process Reactions

Scrubber:

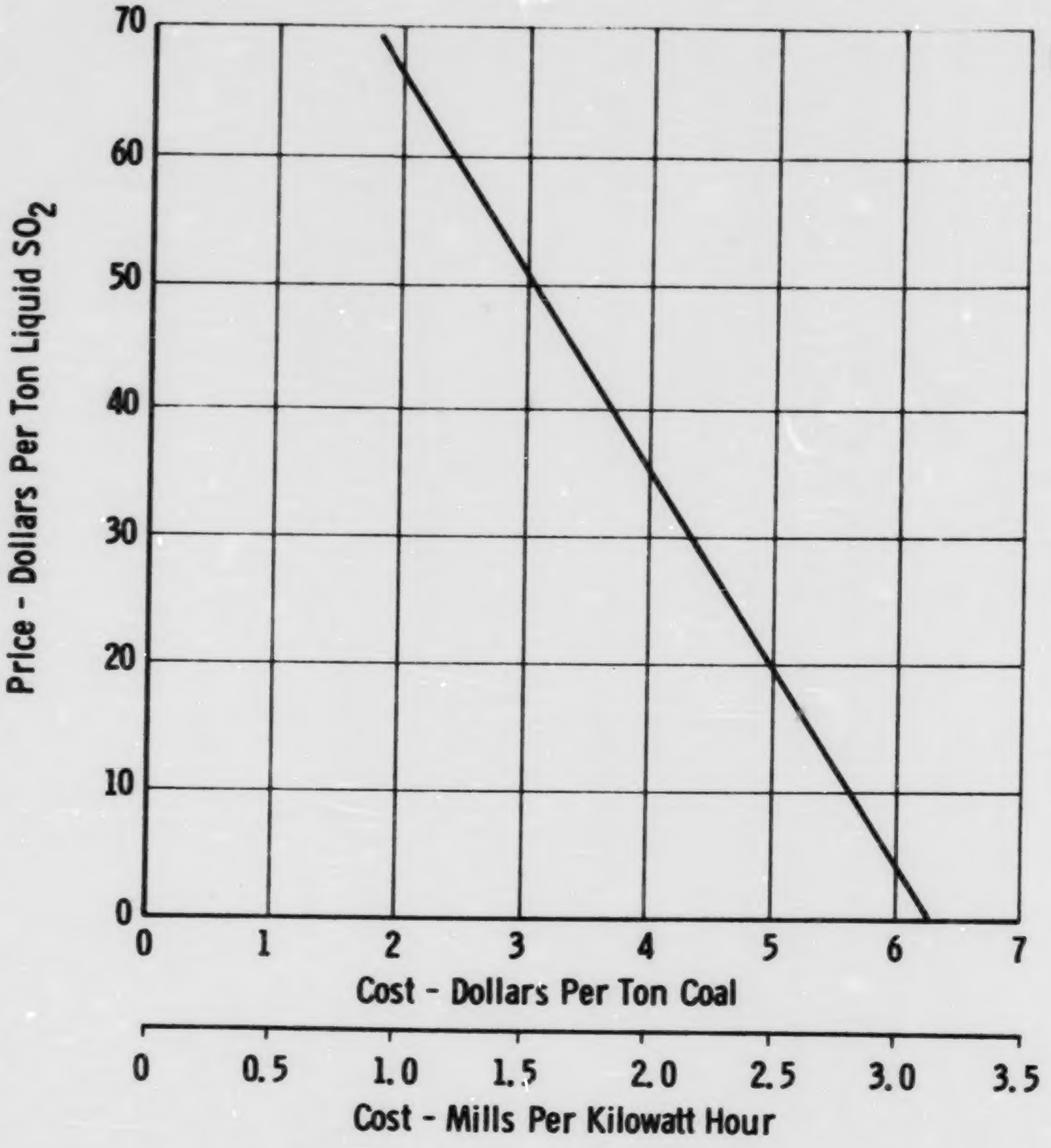
$$SO_2 + MnO_2 \downarrow \longrightarrow MnSO_4$$

$$3\,SO_2 + 1/2\ O_2 + H_2O + MnO_2 \downarrow \longrightarrow H_2SO_4 + MnS_2O_6$$

Calciner:

$$MnSO_4 \xrightarrow[\Delta]{} \text{Mixed Oxides } (MnO_2,\ Mn_2O_3,\ Mn_3O_4,\ MnO) + SO_2 \uparrow$$

$$MnS_2O_6 \xrightarrow[\Delta]{} MnO_2 + 2\,SO_2 \uparrow$$



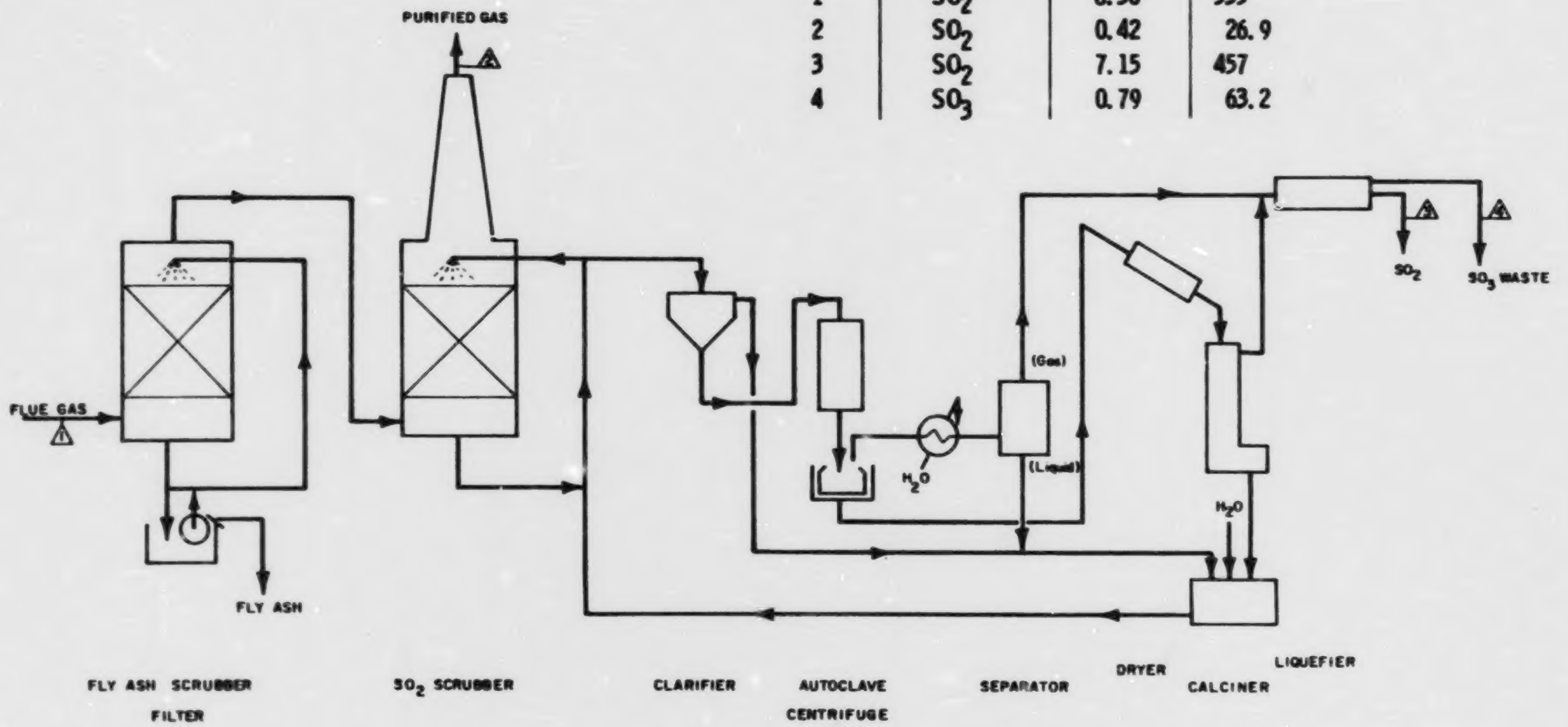
Basis :
- 120 megawatt power plant
- 20 million cfh flue gas
- Sale of 27,165 tons of SO_2 per year

MAGNESIUM OXIDE PROCESS : PROFITABILITY

Figure 17

Reactant Chemicals Per Million SCF Flue Gas Processed

△ Stream	Component	Lb Moles	Lbs
1	SO_2	8.36	535
2	SO_2	0.42	26.9
3	SO_2	7.15	457
4	SO_3	0.79	63.2


PURIFIED GAS
2
FLUE GAS
1
FLY ASH
(Gas)
(Liquid)
H2O
H2O
3
4
SO2
SO3 WASTE
FLY ASH SCRUBBER
FILTER
SO2 SCRUBBER
CLARIFIER
AUTOCLAVE
CENTRIFUGE
SEPARATOR
DRYER
CALCINER
LIQUEFIER

MANGANESE OXIDE PROCESS : FLOW DIAGRAM

Figure 18

Mixer:

$$Mn_2O_3 \downarrow + H_2SO_4 \longrightarrow MnSO_4 + MnO_2 \downarrow + H_2O$$

$$Mn_3O_4 \downarrow + 2\,H_2SO_4 \longrightarrow 2\,MnSO_4 + MnO_2 \downarrow + 2\,H_2O$$

$$MnO \downarrow + H_2SO_4 \longrightarrow MnSO_4 + H_2O$$

(3) Chemical Requirements and By-Product Yields

Table 35 indicates the chemical requirements and by-product yields on treating one million SCF of flue gas by the Manganese Oxide process. The manganese oxides are completely recycled, and theoretically no raw materials are needed.

(4) Cost Estimate

Development of the Manganese Oxide process has been limited. Some pilot-plant studies have been conducted, however. Tarbutton,[424] et al., conducted one investigation, and concluded from a similar method developed by the mining industry[439] that the process is feasible. Equipment similar to the processes investigated by Field, et al., in the Bureau of Mines study[621] was used wherever possible as a basis for the cost estimates in the present study.

(a) Capital Costs

In this process the fly ash in the flue gas must be removed upstream of the SO_2 scrubber. Otherwise the ash would accumulate in the recirculated manganese oxide slurry from which removal would be difficult. A single wood-grid packed, lead-lined steel scrubber with a high water recirculating rate was selected for use as the fly ash scrubber. The Fulham-Simon-Carves scrubber was considered satisfactory for this purpose. Total purchase cost of unit: $231,900.

The design of this tower was based upon the data of Tarbutton which indicate a residence time of 7.5 seconds for complete removal of SO_2 from flue gas, and Vedensky's[439] experience in leaching MnO in a wood-grid packed tower.

TABLE 35

MANGANESE OXIDE PROCESS:

CHEMICAL REQUIREMENTS & BY-PRODUCT YIELDS

	Quantity per Million SCF Flue Gas		Tons per Year		
	Lb Mole	Lb	20 Million SCFH Flue Gas	0.5 Million SCFM Flue Gas	2.5 Million SCFM Flue Gas
Raw Material					
SO_2 (flue gas)	7.94	508	40,230	60,350	301,730
By-Products					
SO_2	7.15	457	36,190	54,280	271,420
SO_3	0.79	63.2	4,910	7,370	36,850

The cost of the 790 sq. ft. by 80 ft. tall Fulham-Simon-Carves scrubber was factored to obtain the cost of the 1,119 sq. ft. by 80 ft. tall scrubber required here, resulting in a cost of $358,300.

A list of other equipment components needed for this process follows:

Autoclave, stainless steel or Monel, 3800 gal, 300 psi, 450°F	$30,800
Clarifiers (2), lead-lined steel	94,000
Filters (4 including spares), vacuum rotary units	83,000
Centrifuge, vertical, perforated-basket, continuous cone-type	63,900
Rotary dryer	46,100
Calciner, 1800°F operating temperature	230,000
Mix tank for MnO_2 slurry	8,060
Swing hammer mill for dried $MnSO_4$ crystals	20,200
Blower for calciner	7,230
Cyclone dust separator (2), one for SO_2 stream and one for flue gas from calciner unit	3,320
Screw conveyors, stainless steel	17,140
Storage bin for $MnSO_4$	29,900
SO_2 liquefaction unit	102,000
	$735,650

The total purchase price of all major equipment for the Manganese Oxide process listed above is $1,325,850. After factoring, the total investment cost becomes $6,908,400 or $57.56 per kilowatt capacity. A capital cost summary for the system is given in Table 36.

TABLE 36

MANGANESE OXIDE PROCESS: CAPITAL COST ESTIMATE SUMMARY

	ITEM	FACTOR	COST - $
1.	Purchased Equipment	1.00	1,326,000
2.	Erection Labor	0.25	331,500
3.	Foundation & Platforms	0.18	238,700
4.	Piping	0.76	1,007,800
5.	Instruments	0.15	198,900
6.	Insulation	0.08	106,100
7.	Electrical	0.10	132,600
8.	Buildings	0.25	331,500
9.	Land & Yard Improvements	0.13	172,400
10.	Utilities	0.40	530,400
11.	Physical-Plant Cost	3.30	4,375,900
12.	Engineering & Construction	0.66	875,100
13.	Direct Plant Cost	3.96	5,251,000
14.	Contractor's Fee	0.19	251,900
15.	Contingency	0.59	782,300
16.	Fixed Capital Cost	4.74	6,285,200
17.	Working Capital, 10%	0.47	623,200
	Total Investment	5.21	6,908,400

18. Capital Requirements
$/kw capacity 57.56

(b) Operating Costs

The annual operating cost was estimated at $2,352,500 equivalent to $4.95/ton of coal and 2.48 mill/kwh. The list of operating costs for the Manganese Oxide process is given in Table 37. Theoretically, there is no make-up requirement for manganese oxide.

The annual direct labor and supervision was assumed to be the same as for the Zinc Oxide process.

The utilities for this process are:

Power:	8,460,000 kwh per year
Steam:	212,000 M lb per year
Make-up Water:	634,000 M gal per year
Fuel Oil:	4,960,000 gal per year

(c) Profitability

The profitability of this system, based on an annual sale of 35,610 tons of liquid SO_2, is given in Figure 19, which indicates a net cost of $3.50/ton of coal with liquid SO_2 selling for $20/ton.

k. Haenisch-Schroeder Process

(1) Process Description

In the Haenisch-Schroeder process,[183] the sulfur dioxide is scrubbed from the flue gas with water. Large quantities of water are required because of the low solubility of the sulfur dioxide. Some lime is continually added to the scrubber effluent in order to precipitate calcium sulfate, formed through oxidation of the sulfur dioxide. A flow diagram is shown in Figure 20.

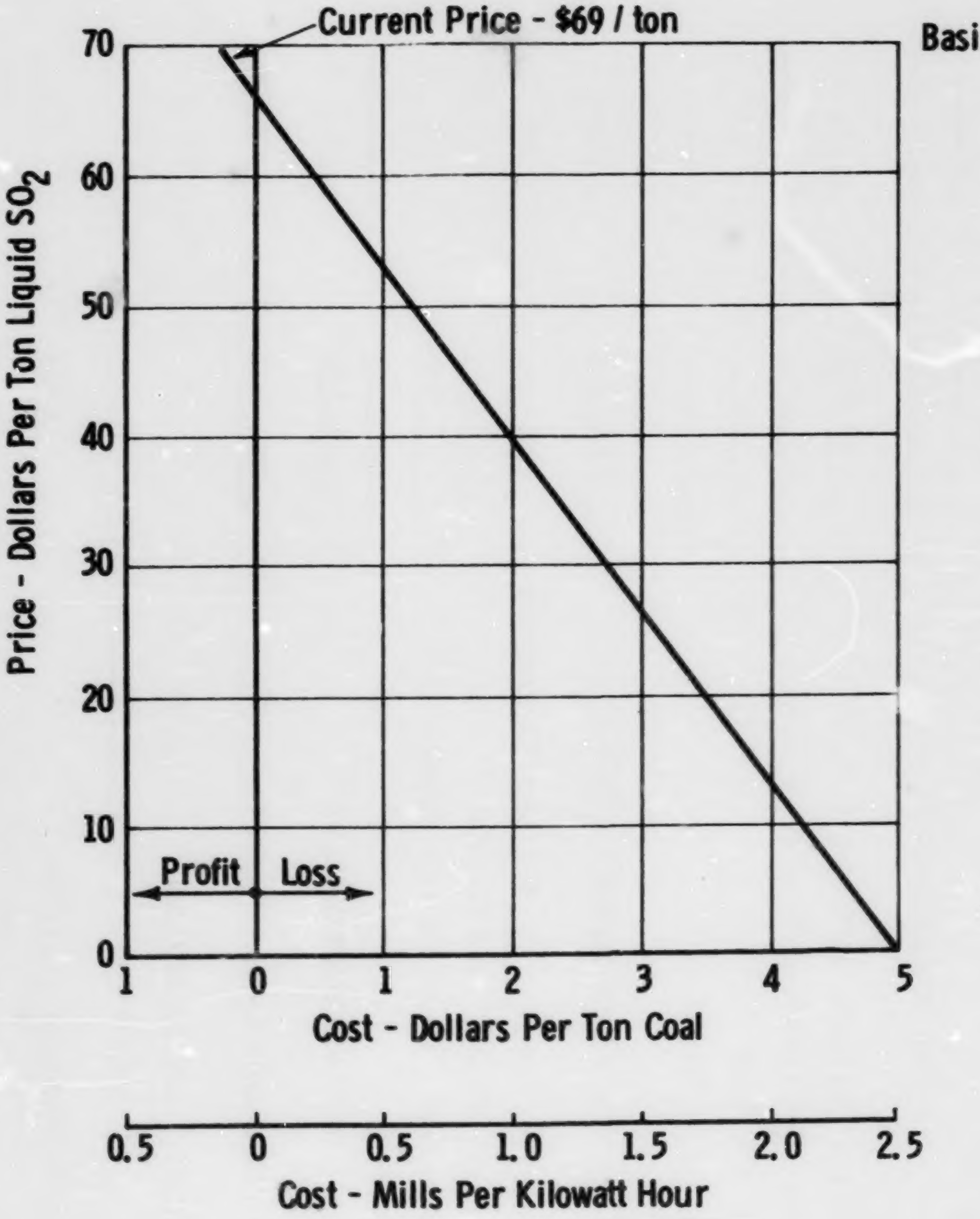
TABLE 37

MANGANESE OXIDE PROCESS: OPERATING COST ESTIMATE SUMMARY

Fixed Capital Cost: $6,285,200

	ITEM	TOTAL $	%
1.	Raw Materials & Chemicals	-	-
2.	Direct Labor	120,000	5.10
3.	Supervision	43,200	1.84
4.	Maintenance, 5% of Fixed Capital	314,200	13.36
5.	Supplies, 15% of Maintenance	47,100	2.00
6.	Utilities	716,000	30.43
7.	Other	-	-
8.	TOTAL DIRECT COST	1,240,500	52.73
9.	Payroll Burden, 20% of 2 & 3	32,600	1.39
10.	Plant Overhead, 50% of 2, 3, 4 & 5	262,300	11.15
11.	Pack & Ship	-	-
12.	Waste Disposal	-	-
13.	Other	-	-
14.	TOTAL INDIRECT COST	294,900	12.54
15.	Depreciation, 10 % Fixed Capital/Yr	628,500	26.72
16.	Taxes, 2% of Fixed Capital	125,700	5.34
17.	Insurance, 1% of Fixed Capital	62,900	2.67
18.	Other	-	-
19.	TOTAL FIXED COST	817,100	34.73
20.	TOTAL OPERATING COST	2,352,500	100.00

21. COST: $/Ton of Coal 4.95
22. Mill/kwh 2.48
23. BY-PRODUCT CREDIT (SEE FIGURE 19)



Basis :
- 120 megawatt power plant
- 20 million cfh flue gas

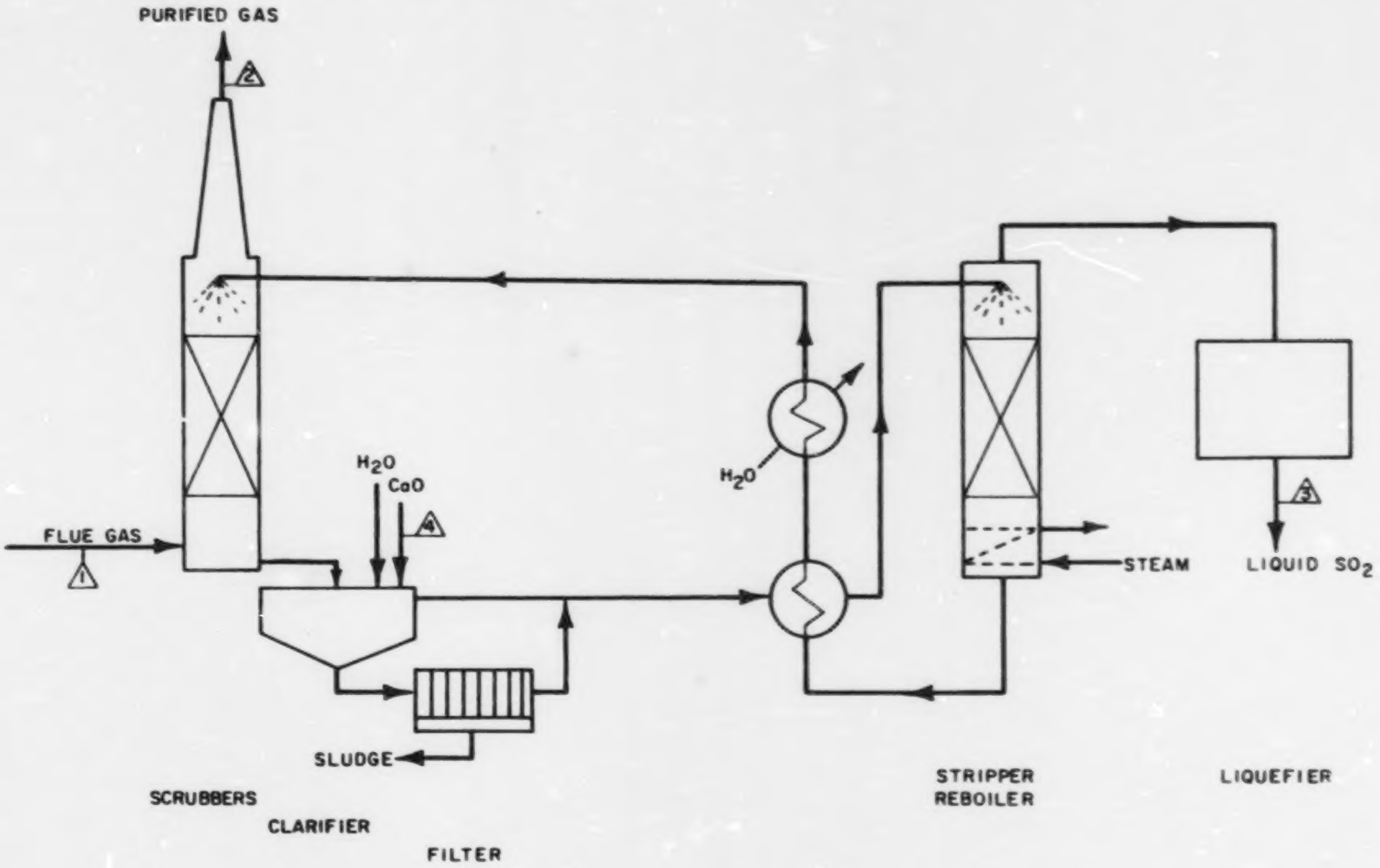
Sale of 35,610 tons SO_2 per year

MANGANESE OXIDE PROCESS : PROFITABILITY

Figure 19

Reactant Chemicals Per Million SCF Flue Gas Processed

△Stream	Component	Lb Moles	Lbs
1	SO_2	8.36	535
2	SO_2	0.42	26.8
3	SO_2	6.83	437
4	CaO	1.11	62.2


PURIFIED GAS
2
FLUE GAS
1
H_2O
CaO
4
SLUDGE
H_2O
STEAM
3
LIQUID SO_2
SCRUBBERS
CLARIFIER
FILTER
STRIPPER
REBOILER
LIQUEFIER

HAENISCH - SCHROEDER PROCESS : FLOW DIAGRAM

Figure 20

(2) Process Reactions

Scrubber:

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

$$H_2O + SO_2 + 1/2\ O_2 \longrightarrow H_2SO_4$$

Clarifier:

$$CaO + H_2SO_4 \longrightarrow CaSO_4 \downarrow + H_2O$$

Stripper:

$$H_2SO_3 \longrightarrow H_2O + SO_2$$

(3) Chemical Requirements and By-Product Yields

Table 38 gives the chemical requirements and by-product yields in treating one million SCF of flue gas by the Haenisch-Schroeder process. Because of the acidic nature of the scrubbing medium, it is assumed that 14% of the SO_2 is oxidized to sulfate. As was pointed out in a previous section which covers the Zinc Oxide process, pilot-plant data have shown that this degree of oxidation does indeed occur in an acid medium.

(4) Cost Estimate

The Haenisch-Schroeder process requires large quantities of water, large-sized equipment, and a high utilities consumption.

(a) Capital Costs

The fixed capital cost for this process of $29,473,000 is very high (see Table 39). Of the purchased equipment cost ($6,218,000), the heat-exchange equipment accounts for about two-thirds of the total. A listing of all of the major equipment follows:

TABLE 38

HAENISCH-SCHROEDER PROCESS:

CHEMICAL REQUIREMENTS & BY-PRODUCT YIELDS

	Quantity per Million SCF Flue Gas		Tons per Year		
	Lb Mole	Lb	20 Million SCFH Flue Gas	0.5 Million SCFM Flue Gas	2.5 Million SCFM Flue Gas
Raw Materials					
SO_2 (flue gas)	7.94	508	40,230	60,350	301,730
CaO	1.11	62.2	4,900	7,400	36,900
By-Products					
SO_2	6.83	437	34,610	51,960	259,800
$CaSO_4$	1.11	151	11,960	17,900	89,500

TABLE 39

HAENISCH-SCHROEDER PROCESS: CAPITAL COST ESTIMATE SUMMARY

	ITEM	FACTOR	COST - $
1.	**Purchased Equipment**	1.00	6,218,000
2.	**Erection Labor**	0.25	1,554,500
3.	**Foundation & Platforms**	0.18	1,119,200
4.	**Piping**	0.76	4,725,800
5.	**Instruments**	0.15	932,700
6.	**Insulation**	0.08	497,400
7.	**Electrical**	0.10	621,800
8.	**Buildings**	0.25	1,554,500
9.	**Land & Yard Improvements**	0.13	808,300
10.	**Utilities**	0.40	2,487,200
11.	**Physical-Plant Cost**	3.30	20,519,400
12.	**Engineering & Construction**	0.66	4,103,900
13.	**Direct Plant Cost**	3.96	24,623,300
14.	**Contractor's Fee**	0.19	1,181,400
15.	**Contingency**	0.59	3,668,600
16.	**Fixed Capital Cost**	4.74	29,473,000
17.	**Working Capital, 10%**	0.47	2,922,000
	Total Investment	5.21	32,395,000

18. **Capital Requirements**
$/kw capacity 269.96

Reboiler for Stripper, 150,000 sq. ft. surface @ \$4.71/sq. ft.	\$709,000
Heat Exchanger, SS tubes, 835,000 sq. ft. surface, @ \$3.50/sq. ft.	2,920,000
Cooler, SS tubes, 124,000 sq. ft. surface, @ \$4.65/sq. ft.	576,000
SO_2 Liquefier, 34,610 tons/year capacity	102,000
Scrubbing Tower, 85.6 ft. x 85.6 ft. x 50 ft. tall, lead-lined steel	405,000
Scrubbing Packing, 12 ft. depth of wood grids, 88,200 cu. ft., @ \$4.31/ft^3	381,000
Blowers (2, 1 spare), 20 MMSCFH, 2.5 in. H_2O static head, 125 hp	32,700
Solution Pumps (8, 2 spares), 45,000 gpm each, 60 ft. head, 900 hp, C.I. centrifugal, SS shaft	116,200
Fly Ash Clarifier, 135,000 gpm overflow, 90,000 sq. ft. surface, 392 ft. dia., 10 ft. deep, concrete	149,000
Filter (2, 1 spare), continuous vacuum-type rotary	41,500
Stripping Column, 85.6 ft. x 85.6 ft. x 50 ft. tall, lead-lined steel	405,000
Stripper Packing, 12 ft. depth of wood grids, 88,200 cu. ft., @ \$4.31/ft^3	381,000
Total purchase equipment:	\$6,218,400

(b) Operating Costs

The estimated annual operating charges are listed in Table 40.

The raw material cost is limited to the cost of the lime used to precipitate the calcium sulfate.

Direct labor is assumed to be 4 men per shift for 4 shifts. Supervision is assumed to be one foreman per shift and one supervisor.

The utilities for the process are:

Steam:	11,820,000 M lbs per year
Power:	33,645,000 kwh per year
Circulating Water:	35,400,000 M gal per year

TABLE 40

HAENISCH-SCHROEDER PROCESS: OPERATING COST ESTIMATE SUMMARY

Fixed Capital Cost: $29,473,000

	ITEM	TOTAL $	%
1.	Raw Materials & Chemicals	76,000	0.52
2.	Direct Labor	72,000	0.50
3.	Supervision	43,200	0.30
4.	Maintenance, 5% of Fixed Capital	1,473,500	10.14
5.	Supplies, 15% of Maintenance	221,000	1.52
6.	Utilities	7,882,000	54.26
7.	Other	-	-
8.	TOTAL DIRECT COST	9,767,700	67.24
9.	Payroll Burden, 20% of 2 & 3	23,000	0.16
10.	Plant Overhead, 50% of 2, 3, 4 & 5	904,800	6.23
11.	Pack & Ship	-	-
12.	Waste Disposal	-	-
13.	Other	-	-
14.	TOTAL INDIRECT COST	927,800	6.39
15.	Depreciation, 10 % Fixed Capital/Yr	2,947,000	20.28
16.	Taxes, 2% of Fixed Capital	589,400	4.06
17.	Insurance, 1% of Fixed Capital	294,700	2.03
18.	Other	-	-
19.	TOTAL FIXED COST	3,831,100	26.37
20.	TOTAL OPERATING COST	14,526,600	100.00

21.	COST: $/Ton of Coal	30.58
22.	Mill/kwh	15.29

23. BY-PRODUCT CREDIT (SEE FIGURE 21)

The total operating cost for the Haenisch-Schroeder process is $14, 526, 000 per year or $30. 58 per ton of coal and 15. 29 mill/kwh.

(c) Profitability

The Haenisch-Schroeder process would operate at a deficiency of $25. 56 per ton of coal burned if all of the SO_2 produced were sold at $69/ton. The deficiency would be even greater (see Figure 21) if the SO_2 had to be sold at lower prices.

1. Wet Thiogen Process

(1) Process Description

The Wet Thiogen process uses water as the absorbent for sulfur dioxide. The scrubber effluent is treated with a solution of barium sulfide to form sulfur and insoluble barium salts. The solids are separated by settling and filtration, dried, and heated to distil off free sulfur. The filtrate, essentially pure water, is returned to the scrubber. The still residue from the sulfur distillation, consisting primarily of barium sulfite and sulfate, is then treated in a furnace to reduce the sulfur compounds to the sulfide which is reused in the process. A flow diagram of the Wet Thiogen process is shown in Figure 22.

(2) Process Reactions

Mixer:

$$\mathrm{2\,BaS + 3\,SO_2 \longrightarrow BaSO_3\downarrow + BaS_2O_3\downarrow + 2\,S\downarrow}$$

$$\mathrm{BaSO_3 + 1/2\;O_2 \longrightarrow BaSO_4\downarrow}$$

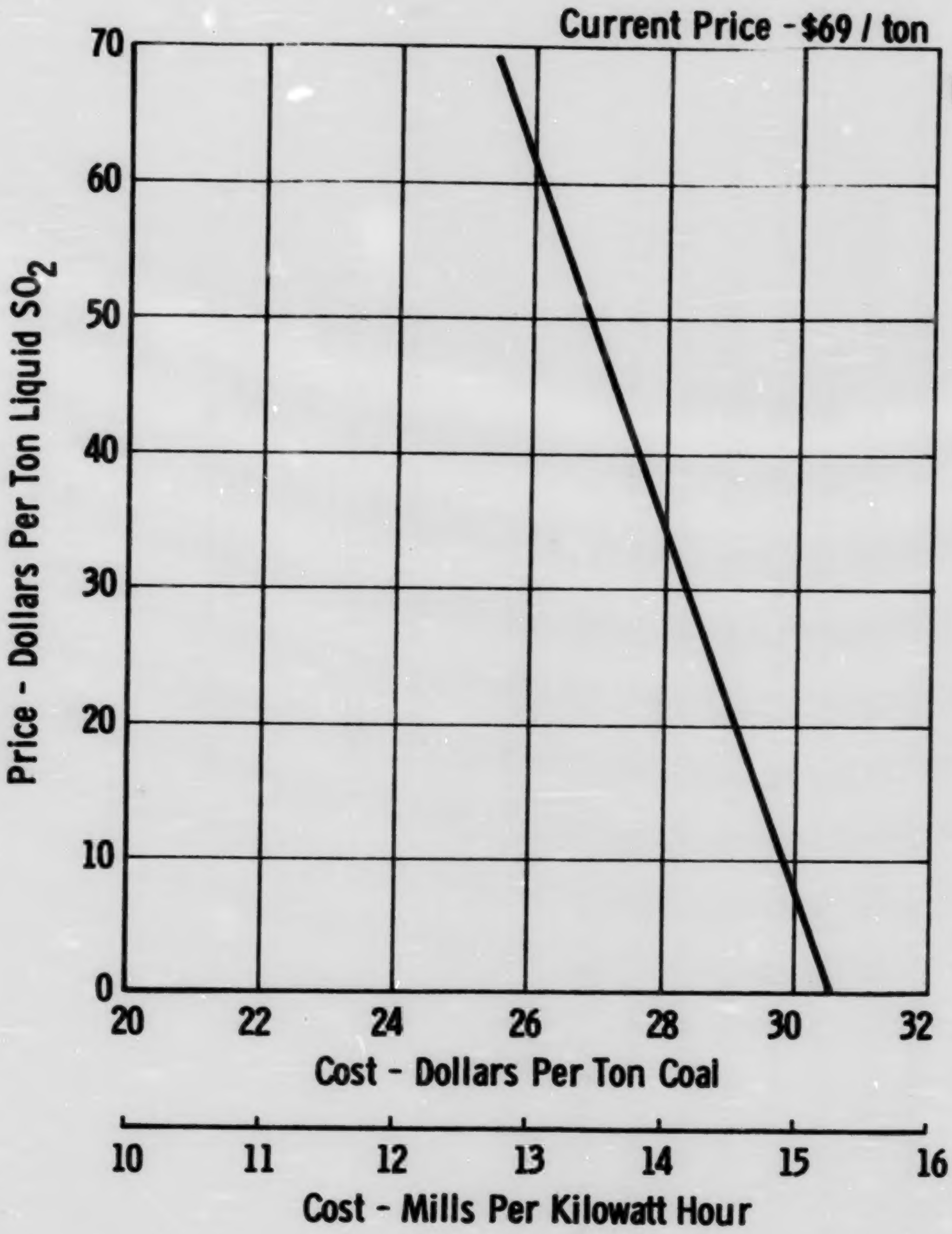
Heater:

$$\mathrm{BaS_2O_3 \xrightarrow{450\text{-}500^{\circ}C} BaSO_3 + S\uparrow}$$

Furnace:

$$\mathrm{BaSO_3 + 3\,C \longrightarrow BaS + 3\,CO\uparrow}$$

$$\mathrm{BaSO_4 + 4\,C \longrightarrow BaS + 4\,CO\uparrow}$$



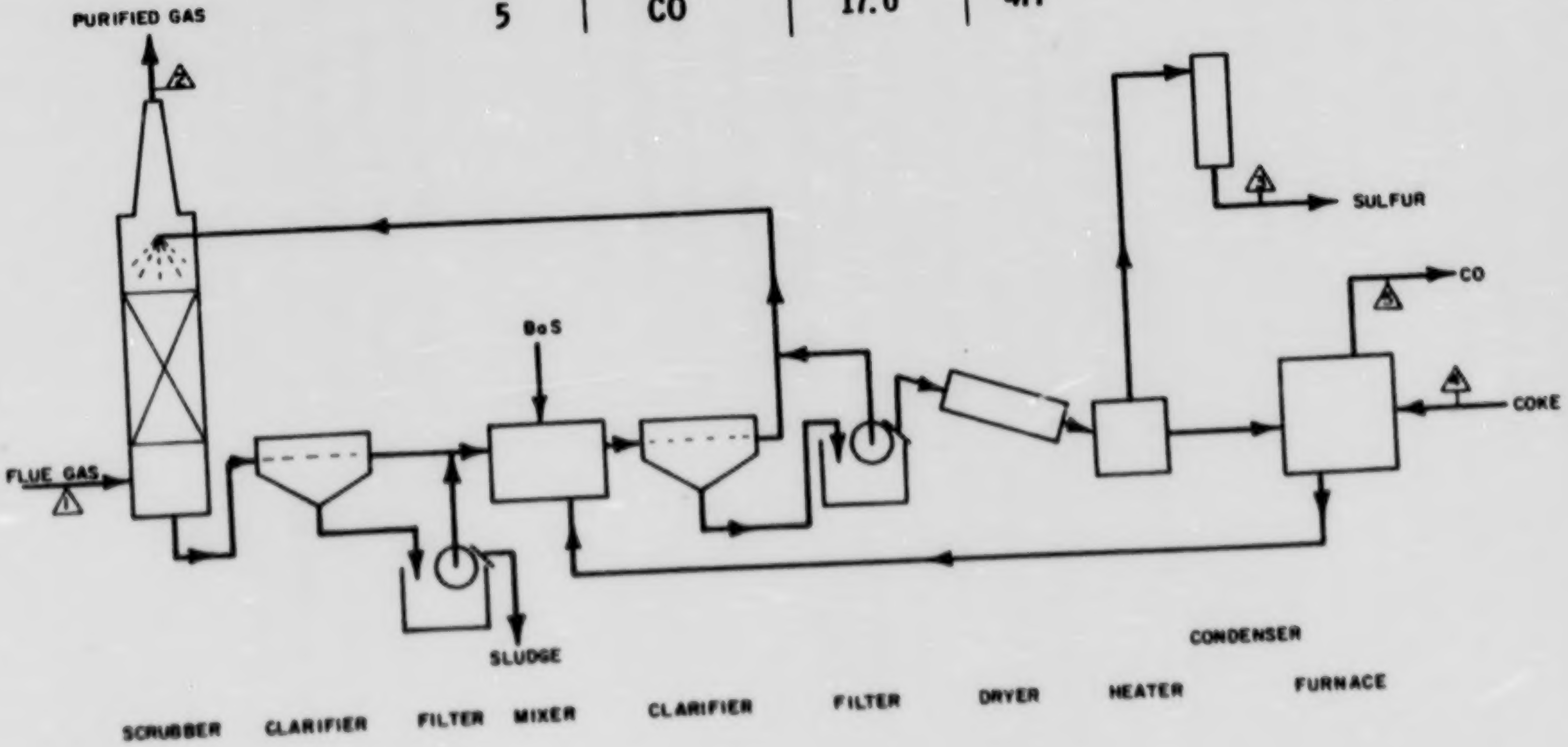
Basis :
- 120 megawatt power plant
- 20 million cfh flue gas
- Sale of 34, 610 tons SO_2 per year

HAENISCH - SCHROEDER PROCESS : PROFITABILITY

Figure 21

Reactant Chemicals Per Million SCF Flue Gas Processed

△ Stream	Component	Lb Moles	Lbs
1	SO_2	8.36	535
2	SO_2	0.42	26.8
3	S	7.94	254
4	C	17.0	205
5	CO	17.0	477


PURIFIED GAS
2
FLUE GAS
1
BaS
SLUDGE
SULFUR
3
CO
5
COKE
4
SCRUBBER
CLARIFIER
FILTER
MIXER
CLARIFIER
FILTER
DRYER
HEATER
CONDENSER
FURNACE

WET THIOGEN PROCESS : FLOW DIAGRAM

Figure 22

(3) Chemical Requirements and By-Product Yields

Table 41 gives the chemical requirements and the by-product yield in treating one million SCF of flue gas by the Wet Thiogen process. Coke is the only raw material consumed in the process and sulfur the only by-product. A quantitative yield of sulfur is assumed since all oxidative products are eventually reduced with coke. The barium sulfide is recycled. The carbon monoxide is not considered as a salable by-product and is discharged through the furnace stack.

(4) Cost Estimate

The Wet Thiogen process was one of the earliest methods for removing SO_2 from smelter gases. Its development was limited, however, the process being abandoned after some pilot-plant work. The absorption section, mixing tank, and solution clarifiers required for flue gas applications are of very large size due to the low SO_2 solubility in water. The remainder of the plant equipment dealing with sulfur recovery and recycle of the barium sulfide was sized according to the quantity of sulfur handled.

For consistency with the many other processes evaluated in this study, the cost of major equipment such as absorption columns, pumps, filters, etc., were taken, whenever possible, from the Bureau of Mines study reported in Reference 621. Other equipment costs were taken from Reference 59.

(a) Capital Costs

The SO_2 scrubber was sized to accommodate the very high water-circulation rate required (135,000 gpm). A lead-lined steel tower with wood-grid packing similar to the Fulham-Simon-Carves tower is used. With a liquid loading of 1100 gph/ft^2, 7350 sq. ft. of tower cross section is required. A 12-ft. depth of packing is used giving a 16-sec. gas-content time in the scrubber.

TABLE 41

WET THIOGEN PROCESS:

CHEMICAL REQUIREMENTS & BY-PRODUCT YIELDS

	Quantity per Million SCF Flue Gas		Tons per Year		
	Lb Mole	Lb	20 Million SCFH Flue Gas	0.5 Million SCFM Flue Gas	2.5 Million SCFM Flue Gas
Raw Materials					
SO_2 (flue gas)	7.94	508	40,230	60,350	301,730
Coke	17.04	204.5	16,200	24,300	121,500
By-Products					
S	7.94	254.1	20,120	30,180	150,900
CO	17.04	477.1	37,790	56,700	283,400

The following scrubber section equipment components are pertinent:

Tower, 85.6 ft. by 85.6 ft., lead-lined steel, 50 ft. tall	$405,000
Packing, wood grids 88,200 ft^3 at $4.31/$ft^3$	381,000
Blowers (2, 1 spare), 20 MMSCFH at 2.5 in. H_2O static head, 125 hp	32,700
Solution Pumps (4, 1 spare), 45,000 gpm each at 60 ft. head, 900 hp, CI centrifugal with SS shafts	58,100
Fly Ash Clarifier, for 135,000 gpm overflow, 90,000 sq. ft. surface, rectangular or 392 ft. dia., 10 ft. deep, concrete	149,000
Fly Ash Filter (2, 1 spare), continuous, vacuum-type rotary	41,500
Total purchase price:	$1,067,300

Other major equipment is listed below:

Mixing Tank, 2-min. hold time, 214-ft. dia. by 10-ft. deep, concrete	$74,500
Solution Clarifier, 135,000 gpm overflow, 392 ft. dia., 10 ft. deep, concrete	149,000
Filters for barium salts and sulfur (3, 1 spare), 500 sq. ft. surface each, continuous vacuum rotary and accessories	97,500
Dryer for barium salts, oil fired, steel, rotary drum	46,000
Heater for barium salts, 850°F, oil fired, steel and brick-lined	115,000
Furnace for reduction of barium salts with coke, oil-fired rotary kiln	172,000
Cyclone for gas-solids separation, stainless steel	3,330
Sulfur condenser and hold tank, 1000 ft^3, concrete tank with cooling coils	15,500
Total purchase price:	$672,830

Total major equipment purchase cost: $1,740,130

After factoring, the total investment becomes $9,065,000 or $75.54 per kilowatt capacity. A capital cost summary for the system is given in Table 42.

(b) Operating Costs

The estimated annual operating costs for the Wet Thiogen process are given in Table 43. The annual cost for coke, the major raw material, is $308,000.

Direct labor was assumed to be the same as for the Fulham-Simon-Carves process, i.e., 5 men per shift for 4 shifts. Supervision was assumed as one foreman per shift and one area superintendent.

The utilities requirements for the Wet Thiogen process are as follows:

Power: 18,300,000 kwh per year
Makeup Water: 93,400 M gal per year
Circulating Water: 14,250 M gal per year
Oil: 4,280,000 gal per year

The total operating cost amounts to $2,916,000 per year or $6.14 per ton of coal and 3.07 mill/kwh.

(c) Profitability

This is a relatively high cost process. If all of the sulfur produced is sold at $38/long ton, the net operating cost is still an expensive $4.71/ton of coal.

TABLE 42

WET THIOGEN PROCESS: CAPITAL COST ESTIMATE SUMMARY

	ITEM		FACTOR	COST - $
1.	Purchased Equipment		1.00	1,740,000
2.	Erection Labor		0.25	435,000
3.	Foundation & Platforms		0.18	313,200
4.	Piping		0.76	1,322,400
5.	Instruments		0.15	261,000
6.	Insulation		0.08	139,200
7.	Electrical		0.10	174,000
8.	Buildings		0.25	435,000
9.	Land & Yard Improvements		0.13	226,200
10.	Utilities		0.40	696,000
11.	Physical-Plant Cost		3.30	5,742,000
12.	Engineering & Construction		0.66	1,148,400
13.	Direct Plant Cost		3.96	6,890,400
14.	Contractor's Fee		0.19	330,600
15.	Contingency		0.59	1,027,000
16.	Fixed Capital Cost		4.74	8,248,000
17.	Working Capital, 10%		0.47	817,000
	Total Investment		5.21	9,065,000
18.	Capital Requirements $/kw capacity	75.54		

TABLE 43

WET THIOGEN PROCESS: OPERATING COST ESTIMATE SUMMARY

Fixed Capital Cost: $8,248,000

	ITEM		TOTAL $	%
1.	Raw Materials & Chemicals		308,000	10.56
2.	Direct Labor		120,000	4.11
3.	Supervision		43,200	1.48
4.	Maintenance, 5% of Fixed Capital		412,000	14.13
5.	Supplies, 15% of Maintenance		61,900	2.12
6.	Utilities		548,000	18.79
7.	Other		-	-
8.	TOTAL DIRECT COST		1,493,100	51.20
9.	Payroll Burden, 20% of 2 & 3		32,600	1.12
10.	Plant Overhead, 50% of 2, 3, 4 & 5		318,500	10.92
11.	Pack & Ship		-	-
12.	Waste Disposal		-	-
13.	Other		-	-
14.	TOTAL INDIRECT COST		351,100	12.04
15.	Depreciation, 10 % Fixed Capital/Yr		824,800	28.28
16.	Taxes, 2% of Fixed Capital		164,900	5.65
17.	Insurance, 1% of Fixed Capital		82,500	2.83
18.	Other		-	-
19.	TOTAL FIXED COST		1,072,200	36.76
20.	TOTAL OPERATING COST		2,916,400	100.00
21.	COST: $/Ton of Coal	6.14		
22.	Mill/kwh	3.07		
23.	BY-PRODUCT CREDIT		680,400	-
24.	ADJUSTED OPERATING COST		2,235,600	-
25.	ADJUSTED COST:			
	$/Ton of Coal	4.71		
	Mill/kwh	2.36		

m. Ozone-Mn Ion and $MnSO_4$ Processes

(1) Process Description

These processes involve the use of manganous ion as an effective catalyst for the oxidation of sulfurous acid to sulfuric acid in aqueous solution. With only the oxygen of the flue gas available as the oxidant, the reaction is slow, and in the Ozone-Mn Ion process ozone is utilized to speed up the reaction. Nevertheless, even under the best conditions, the reaction rate is much slower than the neutralization of sulfur dioxide by the various basic media used in other processes. With a synthetic flue gas, a retention time of 36 seconds for sulfur dioxide in the scrubber appears adequate with the Ozone-Mn Ion process, but with a real flue gas the required time is more than doubled. This may be due in part to the presence of trace quantities of phenols in the gas, which tend to poison the catalyst. For either type of flue gas the retention times would be much longer with the Manganese Sulfate process (without ozone). This latter process will thus be much less attractive economically due to the larger scrubber-design requirements. Therefore, it was not considered in the analysis which is presented in the sections which follow.

Both processes are simple in operation, with the product acid being directly obtained as a side stream from the scrubber. However, the acid concentration never exceeds 40%, and consequently the product has little economic value. A flow diagram of the Ozone-Mn Ion system is presented as Figure 23.

(2) Process Reactions

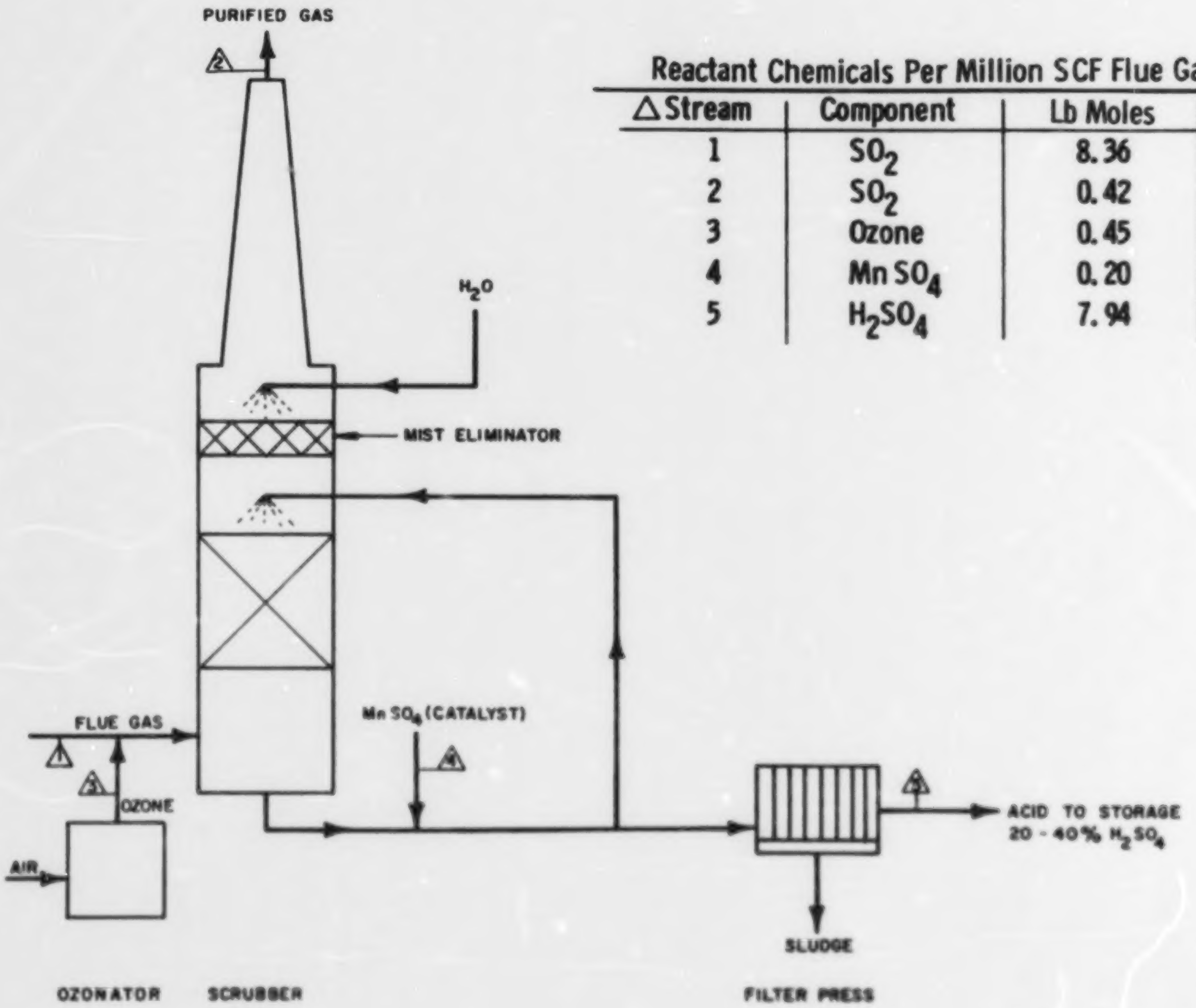
Scrubber:

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

$$H_2SO_3 + O_3 \xrightarrow{Mn^{++}} H_2SO_4 + O_2$$

(3) Chemical Requirements and By-Product Yields

Table 44 shows the raw material and by-product yield requirements for treating one million SCF of flue gas by the Ozone-Mn Ion process. The selected concentrations of chemicals, ozone at 160 ppm in the input gas and Mn^{++} ion at 0.3 g/100 g water in the scrubber liquor, are considered to be adequate for the required degree of SO_2 absorption; these values are based on the results of pilot-plant work at TVA.[424] Although sulfuric acid of approximately 30% strength


PURIFIED GAS
2
H$_2$O
MIST ELIMINATOR
FLUE GAS
1
3
OZONE
AIR
Mn SO$_4$ (CATALYST)
4
5
ACID TO STORAGE
20 - 40% H$_2$SO$_4$
SLUDGE
OZONATOR
SCRUBBER
FILTER PRESS

Reactant Chemicals Per Million SCF Flue Gas Processed

△ Stream	Component	Lb Moles	Lbs
1	SO_2	8.36	535
2	SO_2	0.42	26.8
3	Ozone	0.45	21.6
4	$MnSO_4$	0.20	29.7
5	H_2SO_4	7.94	778

OZONE - Mn ION PROCESS : FLOW DIAGRAM

Figure 23

TABLE 44

OZONE-Mn ION PROCESS:

CHEMICAL REQUIREMENTS & BY-PRODUCT YIELDS

	Quantity per Million SCF Flue Gas		Tons per Year		
	Lb Mole	Lb	20 Million SCFH Flue Gas	0.5 Million SCFM Flue Gas	2.5 Million SCFM Flue Gas
Raw Materials					
SO_2 (flue gas)	7.94	508	40,230	60,350	301,730
$MnSO_4$	0.20	29.7	2,350	3,525	17,625
O_3	0.45	21.6	1,700	2,550	12,750
By-Products					
H_2SO_4 (100%)	7.94	778	61,620	92,430	462,150
(H_2O in 30% Acid)	100	~1800	142,560	213,840	1,069,200

is obtained as a direct by-product, the data in Table 44 lists the 100% acid. Practical considerations indicate that concentration of the acid is perhaps not feasible; nonetheless this optimistic route was taken in order to ascertain whether the process, which is inherently quite unattractive, may have any potential economic merit whatsoever. A subsequent discussion will elaborate on this point.

(4) Cost Estimate

(a) Capital Costs

As mentioned previously, the high retention or reaction time associated with the Ozone-Mn Ion process will result in significant increases in the size and cost of the scrubber. In the Fulham-Simon-Carves process, for example, the scrubbers were designed for a gas velocity of 5 fps through the empty tower; the packing depth was only 6 ft. The lead-lined steel construction of the scrubbers used in the Fulham-Simon-Carves process is suitable to handle the 30-40% sulfuric acid produced in the Ozone-Mn Ion process. Basic cost data therefore was obtained from the Bureau of Mines study in which the Fulham-Simon-Carves process was considered.

In the referenced Bureau of Mines report, the installed scrubber cost was equivalent to $2.66 per cubic foot. Correction to a purchased cost for 1967 gives a value of $2.09/cu. ft. Due to the huge size of the scrubbers required for a 36- to 88-sec. retention time, the velocity through the empty scrubbers was reduced to 1 fps. This would require a tower having a cross-sectional area of nearly 5,600 ft. The total height of a tower containing a 36-ft. column of packing was assumed to be 100 feet (gas entry, liquid distributor, mist eliminator, and gas outlet). Cost of the tower, based on the volume of the unit was calculated to be $1,160,000. The packing and distributor costs were estimated in a similar manner, resulting in a value of $837,000. A tower of this size would probably have little utility. For example, gas and liquid distribution would be a problem. The use of several towers used in parallel and having smaller cross-sectional areas would increase the cost additionally.

It was calculated that the pressure drop in the large tower could be handled by a blower similar to those used in the Fulham-Simon-Carves process. The present cost of two blowers (one stand-by) was estimated at $33,300.

The cost of pumps for circulation of the scrubbing liquor will be higher than might normally be expected due to the need for Carpenter 20 or similar alloy material to insure compatibility with the 30% sulfuric acid. An increase in pumping capacity is also needed because of the high cross-sectional area of the towers. The estimated cost of the pumps was $103,000.

The cost of two filter presses was estimated at $57,000. A 150,000-gal lead-lined storage system for 30% acid was estimated at $45,700. The ozone was charged as a raw material in the operating-cost estimate.

The total purchased equipment cost is $2,236,000 for a system which would provide a 36-sec. retention time in the absorbers. The total investment was estimated to be $11,649,500, or 97.08/kw capacity. See Table 45.

The purchased equipment cost for a system providing an 88-sec. retention time will be substantially higher. If the scrubbing tower and auxiliary equipment priced above are increased in size using the 0.6 factor, these costs become $3,410,000. The blower cost will increase by about 50% to $50,000. All other equipment costs will be the same.

The total purchased equipment cost for a system providing an 88-sec. retention is $3,665,700. It is evident that the indicated fixed capital costs for both systems is excessive. However, the standard factors used for auxiliary equipment may be high since the increase in scrubber size will not necessarily increase the costs of all these components. The total capital cost of $19,098,300 is summarized in Table 46.

(b) Operating Costs

Operating costs for the 36-sec. system are $3,120,500 per year or $6.57/ton of coal and 3.29 mill/kwh; for the 88-sec. system the costs are $4.586.000 per year or $9.65/ton of coal and 4.83 mill/kwh. See Tables 47 and 48.

The raw material quantities shown in Table 44 were used in the analysis. The cost of ozone in 1957 was established at $0.105 per lb;[424] this value was used in the cost analysis although it is expected that the current cost may be somewhat higher.

TABLE 45

OZONE-Mn ION PROCESS: CAPITAL COST ESTIMATE SUMMARY

(36-Sec. Reaction Time)

	ITEM	FACTOR	COST - $
1.	Purchased Equipment	1.00	2,236,000
2.	Erection Labor	0.25	559,000
3.	Foundation & Platforms	0.18	402,500
4.	Piping	0.76	1,699,400
5.	Instruments	0.15	335,400
6.	Insulation	0.08	178,900
7.	Electrical	0.10	223,600
8.	Buildings	0.25	559,000
9.	Land & Yard Improvements	0.13	290,600
10.	Utilities	0.40	894,400
11.	Physical-Plant Cost	3.30	7,378,800
12.	Engineering & Construction	0.66	1,475,800
13.	Direct Plant Cost	3.96	8,854,600
14.	Contractor's Fee	0.19	424,800
15.	Contingency	0.59	1,319,200
16.	Fixed Capital Cost	4.74	10,598,600
17.	Working Capital, 10%	0.47	1,050,900
	Total Investment	5.21	11,649,500
18.	Capital Requirements $/kw capacity 97.08		

TABLE 46

OZONE-Mn ION PROCESS: CAPITAL COST ESTIMATE SUMMARY

(88-Sec. Reaction Time)

	ITEM	FACTOR	COST - $
1.	Purchased Equipment	1.00	3,665,700
2.	Erection Labor	0.25	916,400
3.	Foundation & Platforms	0.18	659,800
4.	Piping	0.76	2,785,900
5.	Instruments	0.15	549,900
6.	Insulation	0.08	293,300
7.	Electrical	0.10	366,600
8.	Buildings	0.25	916,400
9.	Land & Yard Improvements	0.13	476,500
10.	Utilities	0.40	1,466,300
11.	Physical-Plant Cost	3.30	12,096,800
12.	Engineering & Construction	0.66	2,419,400
13.	Direct Plant Cost	3.96	14,516,200
14.	Contractor's Fee	0.19	696,500
15.	Contingency	0.59	2,162,700
16.	Fixed Capital Cost	4.74	17,375,400
17.	Working Capital, 10%	0.47	1,722,900
	Total Investment	5.21	19,098,300

18. Capital Requirements
$/kw capacity 159.15

TABLE 47

OZONE-Mn ION PROCESS: OPERATING COST ESTIMATE SUMMARY
(36-Sec. Reaction Time)

Fixed Capital Cost: $10,598,600

	ITEM		TOTAL $	%
1.	Raw Materials & Chemicals		575,000	18.43
2.	Direct Labor		48,000	1.54
3.	Supervision		43,200	1.38
4.	Maintenance, 5% of Fixed Capital		529,900	16.98
5.	Supplies, 15% of Maintenance		79,500	2.54
6.	Utilities		98,500	3.16
7.	Other		-	-
8.	TOTAL DIRECT COST		1,374,100	44.03
9.	Payroll Burden, 20% of 2 & 3		18,200	0.58
10.	Plant Overhead, 50% of 2, 3, 4 & 5		350,300	11.23
11.	Pack & Ship		-	-
12.	Waste Disposal		-	-
13.	Other		-	-
14.	TOTAL INDIRECT COST		368,500	11.81
15.	Depreciation, 10 % Fixed Capital/Yr		1,059,900	33.97
16.	Taxes, 2% of Fixed Capital		212,000	6.79
17.	Insurance, 1% of Fixed Capital		106,000	3.40
18.	Other		-	-
19.	TOTAL FIXED COST		1,377,900	44.16
20.	TOTAL OPERATING COST		3,120,500	100.00
21.	COST: $/Ton of Coal	6.57		
22.	Mill/kwh	3.29		
23.	BY-PRODUCT CREDIT		NOT APPLIED	

TABLE 48

OZONE-Mn ION PROCESS: OPERATING COST ESTIMATE SUMMARY
(88-Sec. Reaction Time)

Fixed Capital Cost: $17,375,400

	ITEM	TOTAL $	%
1.	Raw Materials & Chemicals	575,000	12.54
2.	Direct Labor	48,000	1.05
3.	Supervision	43,200	0.94
4.	Maintenance, 5% of Fixed Capital	868,800	18.94
5.	Supplies, 15% of Maintenance	130,300	2.84
6.	Utilities	98,500	2.15
7.	Other	-	-
8.	TOTAL DIRECT COST	1,763,800	38.46
9.	Payroll Burden, 20% of 2 & 3	18,200	0.40
10.	Plant Overhead, 50% of 2, 3, 4 & 5	545,200	11.88
11.	Pack & Ship	-	-
12.	Waste Disposal	-	-
13.	Other	-	-
14.	TOTAL INDIRECT COST	563,400	12.28
15.	Depreciation, 10 % Fixed Capital/Yr	1,737,500	37.89
16.	Taxes, 2% of Fixed Capital	347,500	7.58
17.	Insurance, 1% of Fixed Capital	173,800	3.79
18.	Other	-	-
19.	TOTAL FIXED COST	2,258,800	49.26
20.	TOTAL OPERATING COST	4,586,000	100.00

21. COST: $/Ton of Coal 9.65
22. Mill/kwh 4.83

23. BY-PRODUCT CREDIT (SEE FIGURE 24)

Direct labor was estimated at a relatively low level of two men per shift. Supervision of one foreman per shift plus one area supervisor was considered as adequate.

The utility requirements for both variations of this process are as follows:

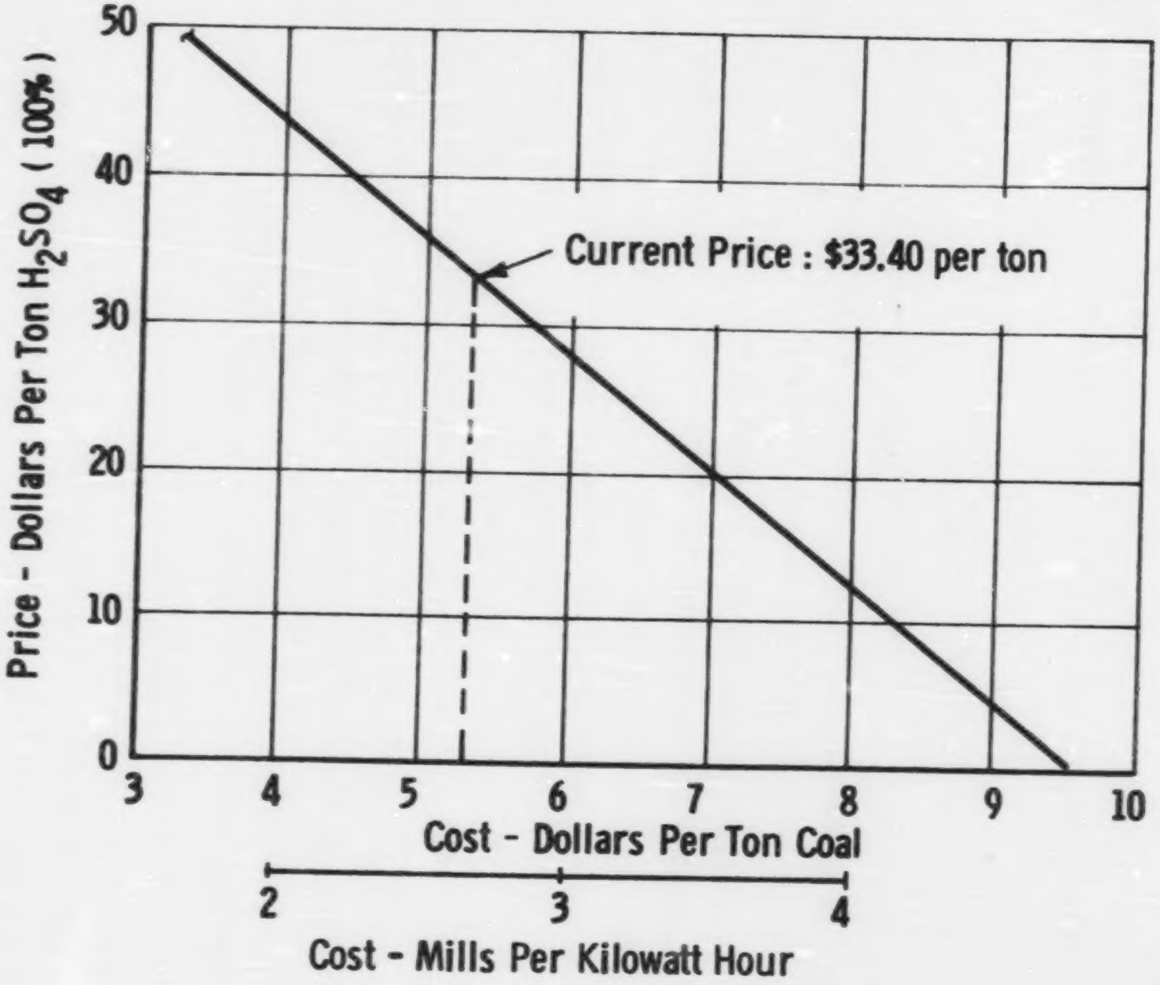
Power:	1,550,000 kwh per year
Makeup Water:	34,200 M gal per year
Circulating Water:	47,500 M gal per year

The operating cost for the system with the 36-sec. reaction time is presented only as a hypothetical case which is not achievable with real flue gas. The operating cost of $9.65 per ton of coal (without by-product credit) for the system having the 88-sec. reaction time was used for comparison with the economic considerations developed for the other processes.

(c) Profitability

The data shown in Table 44 indicate that a substantial quantity of sulfuric acid (approximately 30%) is recoverable as a by-product. It must, however, be concentrated to at least 78% to be commercially valuable. If it were possible to recover the value of this acid (as 100%) at current prices, it would yield an income of $2,058,100. This would reduce operating costs by $4.33 per ton of coal burned. Subtracting this from the $9.65 operating cost shown in Table 48 yields a net operating cost of $5.32 per ton of coal; this value is still very high when compared with the results for some of the other processes.

These cost values would be even higher if the cost of concentrating the acid were included. In a comprehensive study of the method, Johnstone found that acid of strength not exceeding 4% is produced when flue gas from coal combustion is used. Accordingly, the results presented in the foregoing are very optimistic. Because the process is economically uncompetitive, as considered above, no further attempt was made to quantitatively determine what the effect of producing the 4% acid rather than the 30 or 40% product would have on process costs; obviously, the costs would be even higher. Figure 24 shows the optimistic profitability of the process for the conditions specified.



Basis : •120 megawatt power plant
•20 million cfh flue gas
•Sale of 61,620 tons H_2SO_4 (100%) per year

OZONE - Mn ION PROCESS : PROFITABILITY

Figure 24

n. Sulfidine Process

(1) Process Description

In the Sulfidine process a mixture of xylidine and water (approximately 1:1) is used as the absorbent for sulfur dioxide. The absorbent is then stripped of the gas by the use of indirect steam and pure sulfur dioxide is recovered after washing, drying, and compression. The process is complicated by the necessity of scrubbing xylidine vapors from the waste gas by the use of dilute sulfuric acid in a separate scrubbing tower. The xylidine sulfite solution must then be stripped to remove the xylidine. A further complication of the process is the necessity of adding soda ash to the absorption system in order to control the formation of sulfates formed from the oxidation of sulfur dioxide. The resulting sodium sulfate is removed from the system with the waste water stream. A flow diagram of the sulfidine process is given in Figure 25.

(2) Process Reactions

Scrubber:

$$X^{*} + SO_2 + H_2O \longrightarrow (XH)\,HSO_3$$

$$2X + SO_2 + H_2O \longrightarrow (XH)_2SO_3$$

$$(XH)_2SO_3 + 1/2\ O_2 \longrightarrow (XH)_2SO_4$$

$$(XH)_2SO_4 + Na_2CO_3 \longrightarrow 2X + Na_2SO_4 + CO_2 + H_2O$$

Stripper:

$$(XH)\,HSO_3 \longrightarrow X + SO_2 + H_2O$$

$$(XH)_2SO_3 \longrightarrow 2X + SO_2 + H_2O$$

(3) Chemical Requirements and By-Product Yields

Table 49 gives the raw material requirements and by-product yields for treating one million SCF of flue gas by the Sulfidine process. In this process, the extent of SO_2 oxidation in solution was reported by Katz[234] to be one percent for the case of a smelter gas containing 5% SO_2. However,

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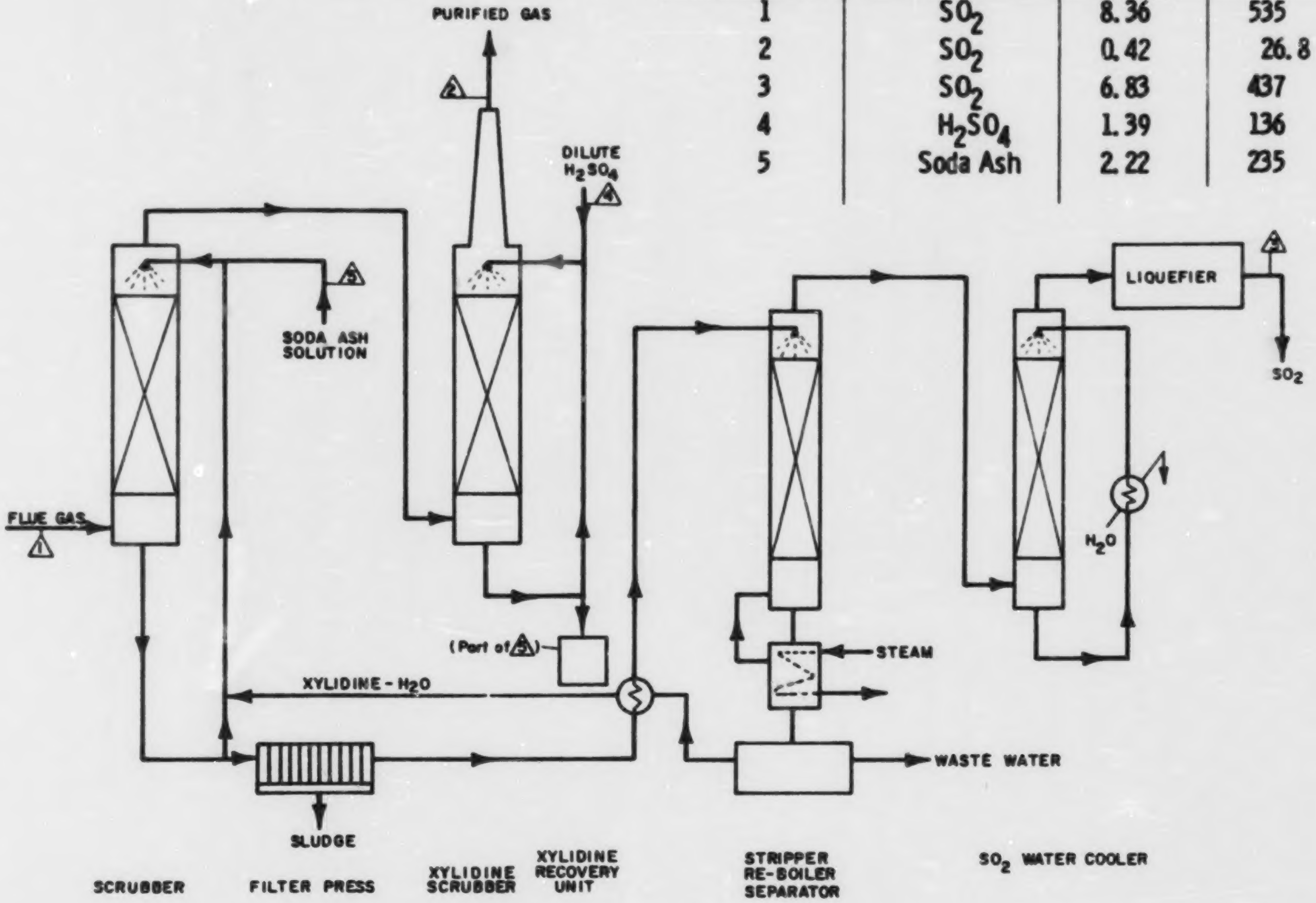
[*] X = mixture of xylidine isomers, $C_6H_3(CH_3)_2NH_2$.

Reactant Chemicals Per Million SCF Flue Gas Processed

△Stream	Component	Lb Moles	Lbs
1	SO_2	8.36	535
2	SO_2	0.42	26.8
3	SO_2	6.83	437
4	H_2SO_4	1.39	136
5	Soda Ash	2.22	235


PURIFIED GAS
2
DILUTE H_2SO_4
4
5
SODA ASH SOLUTION
3
LIQUEFIER
SO_2
FLUE GAS
1
H_2O
(Part of 5)
STEAM
XYLIDINE - H_2O
WASTE WATER
SLUDGE
SCRUBBER
FILTER PRESS
XYLIDINE SCRUBBER
XYLIDINE RECOVERY UNIT
STRIPPER
RE-BOILER
SEPARATOR
SO_2 WATER COOLER

SULFIDINE PROCESS : FLOW DIAGRAM

Figure 25

TABLE 49

SULFIDINE PROCESS:

CHEMICAL REQUIREMENTS & BY-PRODUCT YIELDS

	Quantity per Million SCF Flue Gas		Tons per Year		
	Lb Mole	Lb	20 Million SCFH Flue Gas	0.5 Million SCFM Flue Gas	2.5 Million SCFM Flue Gas
Raw Materials					
SO_2 (flue gas)	7.94	508	40,230	60,350	301,730
H_2SO_4 (100%)	1.39	136	10,740	16,110	80,550
Na_2CO_3	2.22	235	18,610	27,915	139,580
Xylidine, $C_6H_3(CH_3)_2NH_2$	0.165	20	1,580	2,370	11,850
By-Products					
SO_2	6.83	437	34,610	51,960	259,800
Na_2SO_4	2.22	595	47,120	70,680	353,400

Fleming[145] found that the oxidation was much higher for low concentration SO_2 gases. Literature data[672] indicate that the extent of oxidation is essentially independent of the initial SO_2 concentration in the gas. In order to be consistent with the Zinc Oxide process, which was discussed in a previous section, and for which oxidation data are available, 14% of the SO_2 absorbed was assumed to be oxidized in this process. The loss of xylidine as vapor from the scrubbing column and in the various liquid streams had to be considered in this process, since it is a significant item of cost. Data for plants treating 4 or 5% SO_2 gas were extrapolated to a flue gas containing 0.3% SO_2. The xylidine loss of 20 lb/MMSCF flue gas, although quite high, is believed to be conservative for this process. The chemical requirements are based on an absorption temperature of 30°C.

(4) Cost Estimate

In order to be as consistent as possible with the cost estimates conducted for the other processes, a continuing effort was made to utilize the same cost bases to the fullest extent possible. In this particular case, most of the equipment costs for the Sulfidine process were based on the Bureau of Mines cost estimates for the Fulham-Simon-Carves, the Zinc Oxide, and the Howden-I. C. I. (Cyclic Lime) processes. Equipment costs shown herein were corrected to 1967 purchase costs and adjusted for size according to the 0.6 power factor.

(a) Capital Costs

The fixed capital cost for this process of \$10,512,900 is high (see Table 50). Of the total purchased equipment cost of \$2,217,900, more than half (\$1,227,000) reflects the cost of the three main gas scrubbers, packing, and liquid pumps. These large columns, with a cross-sectional area greater than 2,200 square feet, have a liquid capacity of 36,000 gpm. A moderately slow gas-absorption rate (about 10 seconds contact time) further contributes to these large dimensions. Lead-lined steel towers with wood packings similar to the tower used in the Fulham-Simon-Carves process were considered. The heat exchanger cost of \$478,000 constitutes another major cost item; this exchanger of Type 316 stainless steel is required to transfer heat to the 1,750 gpm of corrosive SO_2-rich solution from the hot, lean, stripping column solution. The cost of the SO_2 liquefaction system is \$102,000.

TABLE 50

SULFIDINE PROCESS: CAPITAL COST ESTIMATE SUMMARY

	ITEM	FACTOR	COST - $
1.	Purchased Equipment	1.00	2,217,900
2.	Erection Labor	0.25	554,500
3.	Foundation & Platforms	0.18	399,200
4.	Piping	0.76	1,685,600
5.	Instruments	0.15	332,700
6.	Insulation	0.08	177,400
7.	Electrical	0.10	221,800
8.	Buildings	0.25	554,500
9.	Land & Yard Improvements	0.13	288,300
10.	Utilities	0.40	887,200
11.	Physical-Plant Cost	3.30	7,319,100
12.	Engineering & Construction	0.66	1,463,800
13.	Direct Plant Cost	3.96	8,782,900
14.	Contractor's Fee	0.19	421,400
15.	Contingency	0.59	1,308,600
16.	Fixed Capital Cost	4.74	10,512,900
17.	Working Capital, 10%	0.47	1,042,400
	Total Investment	5.21	11,555,300
18.	Capital Requirements		
	$/kw capacity 96.29		

(b) Operating Costs

The estimated annual operating charges are listed in Table 51. The total operating cost of \$5,803,000 per year, or \$12.22 per ton of coal, is quite high when compared with operating costs of other processes. The largest single item contributing to cost is xylidine, commercially available in tonnage lots as a mixture of the isomers.

The cost of utilities is also relatively high with steam being the most expensive item. This high cost is due to the large molar ratio of steam in SO_2 (30/1) used in the stripping column. The fact that the SO_2 content in the inlet flue gas (0.3%) is low, combined with the need of using large quantities of scrubbing solution, results in a low SO_2 concentration (12.9 g/liter) in the rich solution. These considerations, in addition to the fact that the SO_2 vapor pressure of the xylidine-water solution does not change significantly as the temperature is raised from 30 to 100°C, accounts for the large steam requirement. The utilities for the SO_2 liquefaction system was estimated at \$31,800. Disposal cost of the waste sodium sulfate was based on the weight of the crystalline material.

(c) Profitability

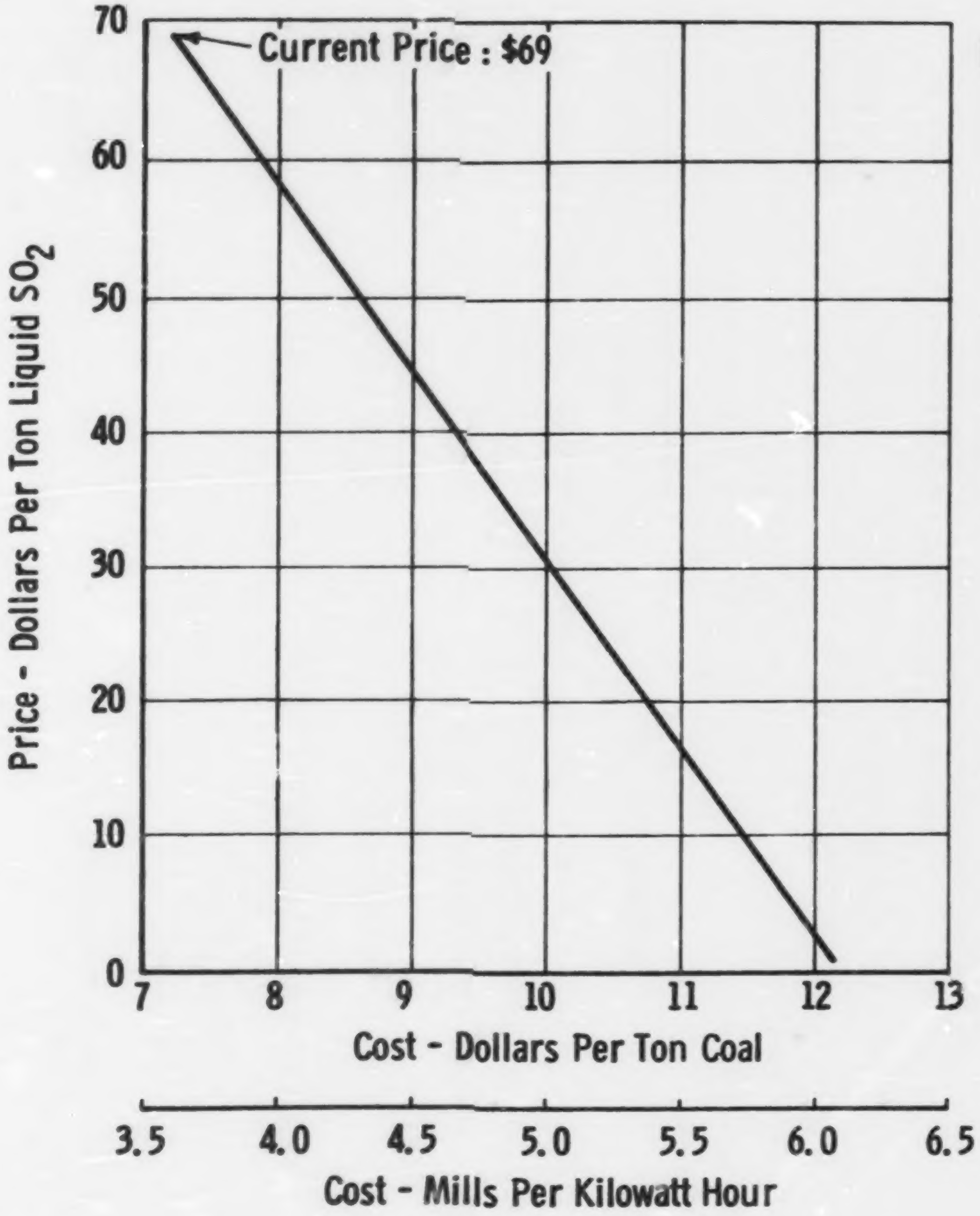
The Sulfidine process would operate at a deficit of \$7.19 per ton of coal burned (see Figure 26), if all of the SO_2 produced were sold for \$69/ton. If the more realistic price of \$19/ton (equivalent sulfur value) was used for all the SO_2 produced, the process would operate at a cost of \$10.75/ton of coal burned. In calculating the above costs, no charges were made to cool the inlet gas to 30°C. In all other processes the gas absorption was assumed to take place at 50°C. This additional cooling would take additional heat-transfer surface and cooling water and further increase the plant costs.

TABLE 51

SULFIDINE PROCESS: OPERATING COST ESTIMATE SUMMARY

Fixed Capital Cost: $10,512,900

	ITEM		TOTAL $	%
1.	Raw Materials & Chemicals		2,422,000	41.73
2.	Direct Labor		120,000	2.07
3.	Supervision		43,200	0.74
4.	Maintenance, 5% of Fixed Capital		525,600	9.06
5.	Supplies, 15% of Maintenance		78,800	1.36
6.	Utilities		641,800	11.06
7.	Other		-	-
8.	TOTAL DIRECT COST		3,831,400	66.02
9.	Payroll Burden, 20% of 2 & 3		32,600	0.56
10.	Plant Overhead, 50% of 2, 3, 4 & 5		383,800	6.62
11.	Pack & Ship		-	-
12.	Waste Disposal		188,500	3.25
13.	Other		-	-
14.	TOTAL INDIRECT COST		604,900	10.43
15.	Depreciation, 10 % Fixed Capital/Yr		1,051,300	18.12
16.	Taxes, 2% of Fixed Capital		210,300	3.62
17.	Insurance, 1% of Fixed Capital		105,100	1.81
18.	Other		-	-
19.	TOTAL FIXED COST		1,366,700	23.55
20.	TOTAL OPERATING COST		5,803,000	100.00
21.	COST: $/Ton of Coal	12.22		
22.	Mill/kwh	6.11		
23.	BY-PRODUCT CREDIT		(SEE FIGURE 26)	



Basis : •120 megawatt power plant
•20 million cfh flue gas
•Sale of 34,610 tons SO_2 per year

SULFIDINE PROCESS : PROFITABILITY
Figure 26

o. Basic Aluminum Sulfate Process

(1) Process Description

The Basic Aluminum Sulfate process involves the absorption of sulfur dioxide with a solution of a soluble basic aluminum salt, followed by thermal stripping of the sulfur dioxide and recycling of the regenerated scrubber liquor. The choice of the absorbing medium is based on the ease with which it can be regenerated in the stripping step. In common with other regenerative methods, oxidation of sulfite to sulfate represents a process complication. In the present process, sulfate is removed as insoluble calcium sulfate through treatment with limestone. A flow diagram of the Basic Aluminum Sulfate process is shown in Figure 27.

(2) Process Reactions

Scrubber:

$$Al(OH)SO_4 + SO_2 \longrightarrow Al(OSO_2H)SO_4$$

$$Al(OSO_2H)SO_4 + 1/2\ O_2 \longrightarrow Al(OSO_3H)SO_4$$

Stripper:

$$Al(OSO_2H)SO_4 \longrightarrow Al(OH)SO_4 + SO_2\uparrow$$

Mixing Vessel:

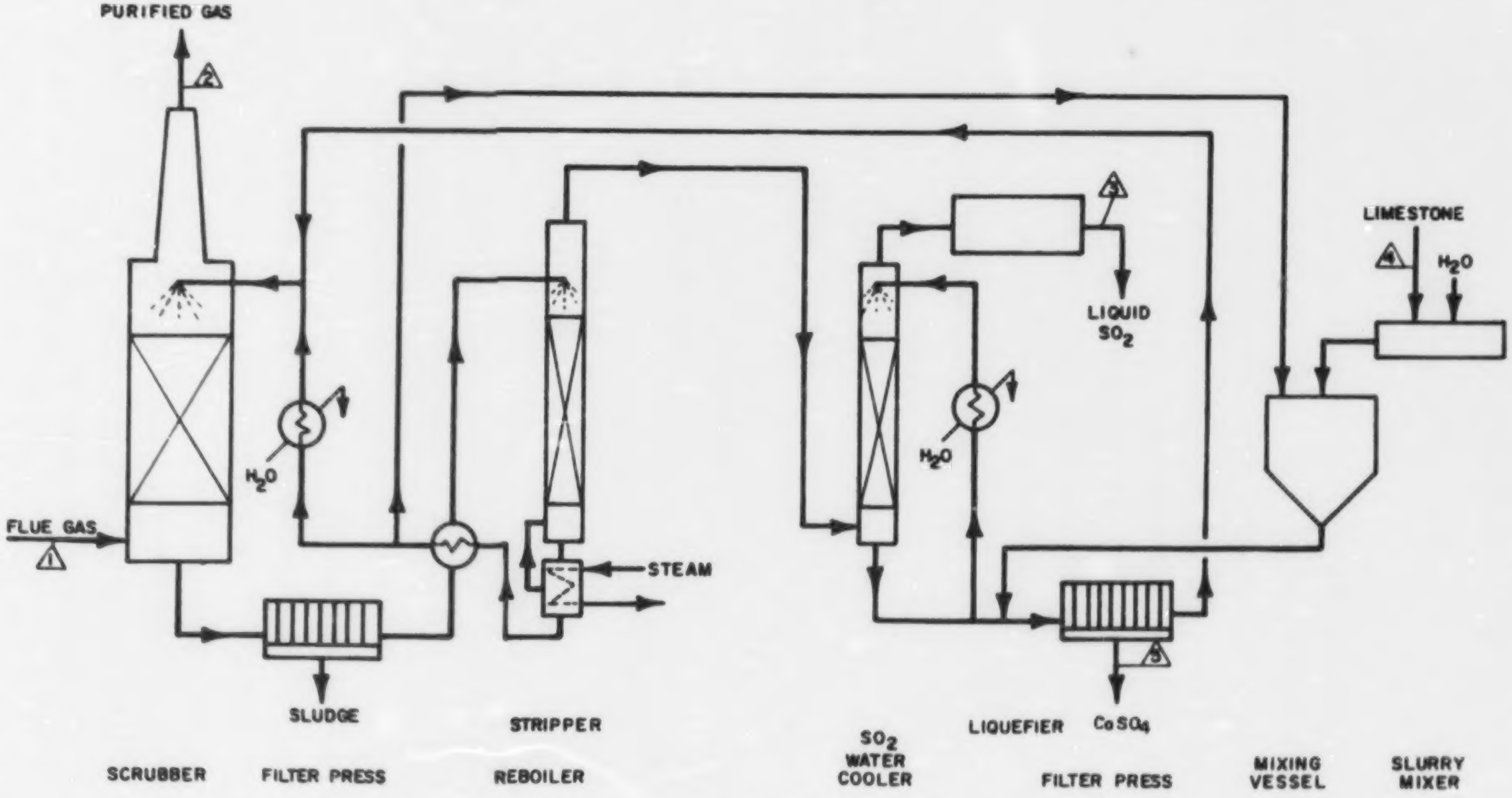
$$CaCO_3 + Al(OSO_3H)SO_4 \longrightarrow CaSO_4\downarrow + CO_2\uparrow - Al(OH)SO_4$$

(3) Chemical Requirements and By-Product Yields

Table 52 gives the raw material and by-product data for treating one million SCF of flue gas by the Basic Aluminum Sulfate process. In smelter-plant applications of this process, 1 to 1-1/2% of the SO_2 absorbed from a 5% feed gas is oxidized to sulfate in solution. As discussed previously in conjunction with the Sulfidine process, however, the extent of oxidation is much higher for low concentration SO_2 gases. In order to be consistent with several other processes for which oxidation data are available, 14% of the SO_2 absorbed is assumed to be oxidized to sulfate.

Reactant Chemicals Per Million SCF Flue Gas Processed

△Stream	Component	Lb Moles	Lbs
1	SO_2	8.36	535
2	SO_2	0.42	26.8
3	SO_2	6.83	437
4	Limestone	1.11	116
5	$CaSO_4 \cdot 2H_2O$	1.11	190


PURIFIED GAS
2
FLUE GAS
1
H_2O
STEAM
H_2O
3
LIQUID SO_2
LIMESTONE
4
H_2O
5
SLUDGE
STRIPPER
LIQUEFIER
$CaSO_4$
SCRUBBER
FILTER PRESS
REBOILER
SO_2 WATER COOLER
FILTER PRESS
MIXING VESSEL
SLURRY MIXER

BASIC ALUMINUM SULFATE PROCESS : FLOW DIAGRAM
Figure 27

TABLE 52

BASIC ALUMINUM SULFATE PROCESS: CHEMICAL REQUIREMENTS AND BY-PRODUCT YIELDS

	Quantity per Million SCF Flue Gas		Tons per Year		
	Lb Mole	Lb	20 Million SCFH Flue Gas	0.5 Million SCFM Flue Gas	2.5 Million SCFM Flue Gas
Raw Materials					
SO_2 (flue gas)	7.94	508	40,230	60,350	301,730
Limestone	1.11	116[a]	9,190	13,780	68,900
By-Products					
SO_2	6.83	437	34,610	51,960	259,800
$CaSO_4$	1.11	190	20,940[b]	31,410[b]	157,050[b]

---

[a] Based on 95% $CaCO_3$ in limestone.

[b] Includes 5% waste rock in limestone and 35% water in filter cake.

Ground limestone is the only major chemical requirement for this process. The calcium sulfate produced is considered to be a waste product and is discarded. In practice, a small quantity of the basic aluminum salt must be added periodically to make up for mechanical losses and losses in the filter cake. Also, a small amount of phosphoric acid may have to be added to the solution occasionally to prevent the crystallization of aluminum sulfate. The quantities of these chemicals are small and therefore they have been classified as in-plant losses not accounted for in this process economic study.

(4) Cost Estimate

In order to be consistent with many of the other processes evaluated in this study, the cost of major equipment such as absorption columns, pumps, and blowers have been taken, whenever possible, from the Bureau of Mines study.[621] These costs were adjusted to 1967 purchase costs, and were adjusted for size according to the 0.6 power factor. Other equipment costs were derived from Chemical Engineering Costs of Process Equipment[59] files.

(a) Capital Costs

The purchased cost of major equipment for this process, \$3,110,000, results in an extremely high total investment of \$16,203,100, or \$135.03/kw capacity. See Table 53.

The largest major equipment cost is for four lead-lined steel absorption towers with wood-grid packing (\$1,731,000). These towers were sized based upon the data of Appleby[10] for the 52 ton/day Imatra, Finland, smelter plant which treated waste gases containing 5% SO_2. The large absorbers are required because of the very small driving force which results from the low concentration of the SO_2 in the gas stream, resulting in a low equilibrium partial pressure of the SO_2 in the scrubbing solution.

A large volume of the scrubber effluent (5,640 gpm) is heated to 100°C, stripped with a large quantity of steam, and then cooled to 50°C for absorption. This requires the following large and expensive heat transfer equipment:

TABLE 53

BASIC ALUMINUM SULFATE PROCESS: CAPITAL COST ESTIMATE SUMMARY

	ITEM	FACTOR	COST - $
1.	Purchased Equipment	1.00	3,110,000
2.	Erection Labor	0.25	777,500
3.	Foundation & Platforms	0.18	559,800
4.	Piping	0.76	2,363,600
5.	Instruments	0.15	466,500
6.	Insulation	0.08	248,800
7.	Electrical	0.10	311,000
8.	Buildings	0.25	777,500
9.	Land & Yard Improvements	0.13	404,300
10.	Utilities	0.40	1,244,000
11.	Physical-Plant Cost	3.30	10,263,000
12.	Engineering & Construction	0.66	2,052,600
13.	Direct Plant Cost	3.96	12,315,600
14.	Contractor's Fee	0.19	590,900
15.	Contingency	0.59	1,834,900
16.	Fixed Capital Cost	4.74	14,741,400
17.	Working Capital, 10%	0.47	1,461,700
	Total Investment	5.21	16,203,100

18. **Capital Requirements**
$/kw capacity 135.03

Heat exchanger, shell and tube, stainless steel tubes, 194,500,000 Btu/hr duty, 194,000 sq. ft. area	$683,000
Reboiler for stripping column, kettle type, stainless steel tubes, 133,300,000 Btu/hr duty, 13,330 sq. ft. at $12.40/ft^2	165,000
Cooler for lean solution, shell and tube, stainless steel tubes, 55,500,000 Btu/hr duty, 15,000 sq. ft. at $8.71/ft^2	131,000
Stripper overhead condenser, shell and tube, stainless steel tubes, 78,700,000 Btu/hr duty, 3850 sq. ft. at $8.71/ft^2	34,000
Total cost of heat exchange equipment:	$1,013,000

Other major equipment items are:

Absorption towers (4), lead lined	$1,731,000
Solution pumps (9, 3 spare), centrifugal, C.I. with SS shafts, 5,640 gpm at 80 ft. head	38,000
Stripping column, lead-lined steel, 6 ft. OD, 50 ft. high	39,000
Storage tanks (6), lead-lined steel, 60,000 gal capacity	100,000
Filter presses (2), for scrubber effluent, lead-lined, pressure type, 479 sq. ft.	58,000
Filter presses (2), for $CaSO_4$, steel, pressure type, 479 sq. ft.	29,000
Liquefaction system, for SO_2	102,000
Total cost of miscellaneous items:	$2,097,000

Total major equipment cost: $3,110,000

(b) Operating Costs

The estimated annual operating charges are listed in Table 54. The total operating cost is $4,070,300 or $8.56 per ton of coal. The raw material and chemical cost for this process is relatively low. The direct labor charge includes the labor required for the SO_2 liquefaction system.

TABLE 54

BASIC ALUMINUM SULFATE PROCESS: OPERATING COST ESTIMATE SUMMARY

Fixed Capital Cost: $14,741,400

	ITEM		TOTAL $	%
1.	Raw Materials & Chemicals		91,900	2.26
2.	Direct Labor		120,000	2.95
3.	Supervision		43,200	1.06
4.	Maintenance, 5% of Fixed Capital		737,100	18.11
5.	Supplies, 15% of Maintenance		110,500	2.71
6.	Utilities		828,000	20.34
7.	Other		-	-
8.	TOTAL DIRECT COST		1,930,700	47.43
9.	Payroll Burden, 20% of 2 & 3		32,600	0.80
10.	Plant Overhead, 50% of 2, 3, 4 & 5		505,400	12.42
11.	Pack & Ship		-	-
12.	Waste Disposal		83,300	2.05
13.	Other		-	-
14.	TOTAL INDIRECT COST		621,300	15.27
15.	Depreciation, 10 % Fixed Capital/Yr		1,474,100	36.22
16.	Taxes, 2% of Fixed Capital		29,500	0.72
17.	Insurance, 1% of Fixed Capital		14,700	0.36
18.	Other		-	-
19.	TOTAL FIXED COST		1,518,300	37.30
20.	TOTAL OPERATING COST		4,070,300	100.00
21.	COST: $/Ton of Coal	8.56		
22.	Mill/kwh	4.28		
23.	BY-PRODUCT CREDIT		(SEE FIGURE 28)	

The cost of utilities is $828,000 per year. This high cost is reflected by the large amount of steam required to strip the SO_2 from the rich solution (25 moles steam per mole SO_2 stripped). Also, a large quantity of water is required to cool the lean solution and condense the stripping steam. The utility requirements follow:

Steam:	1,052,000 M lbs per year
Circulating Water:	3,850,000 M gal per year

The $CaSO_4$ waste amounts to 14,970 tons per year. Adding the 5% waste rock present in the limestone and the water in the filter cake (assumed to be 35%), the total waste tonnage is 20,830 tons.

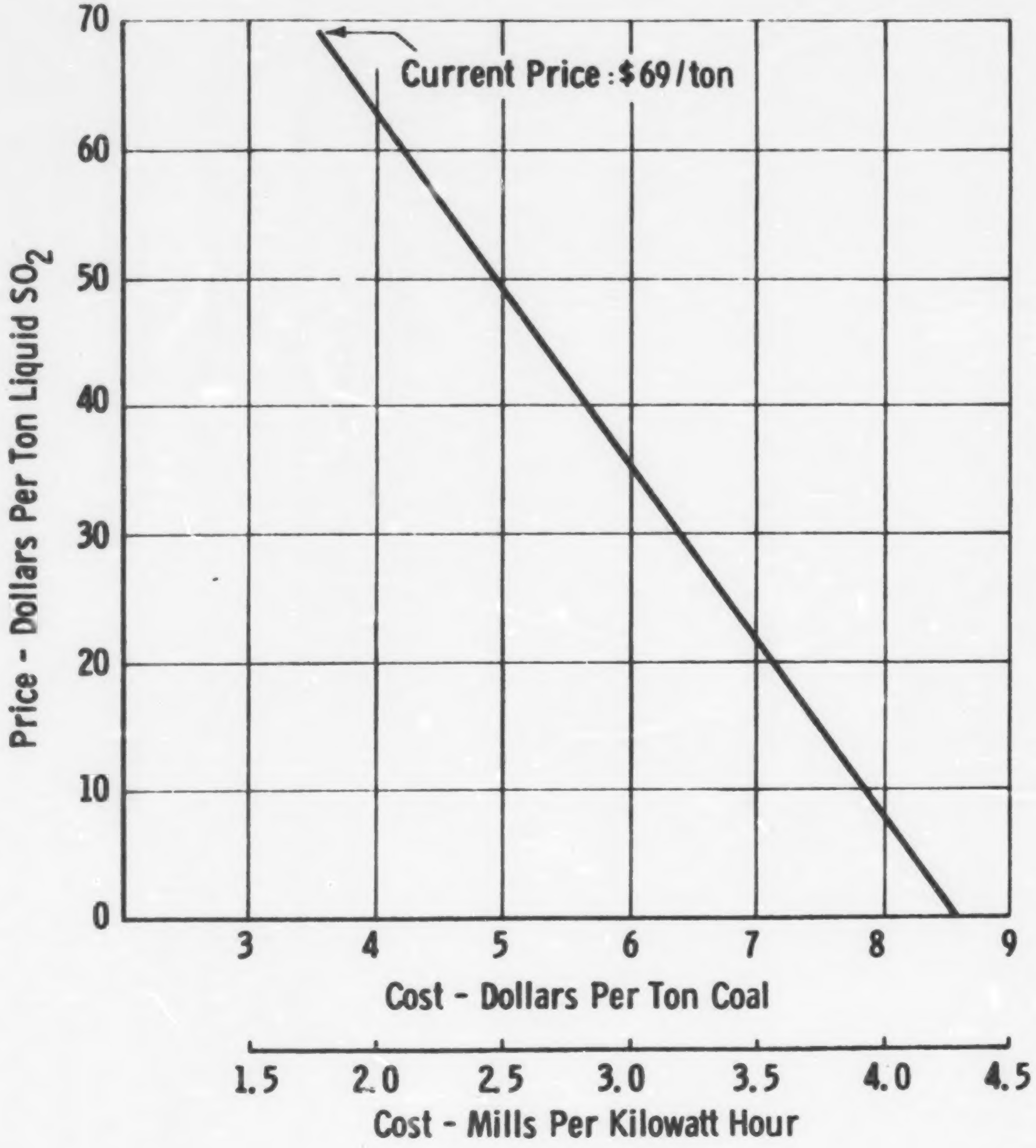
(c) Profitability

Profitability data for the Basic Aluminum Sulfate process are given in Figure 28 which indicates a high cost operation.

p. Ammonia-Hydrazine Process

(1) Process Description

The Ammonia-Hydrazine process involves the scrubbing of flue gas with an aqueous solution of hydrazine salts, including the sulfite and bisulfite. Aqueous hydrazine is added to the circulating scrubber liquor at a rate corresponding to the rate of sulfur dioxide absorption, and a portion of the circulating stream is continuously removed for product recovery. The latter involves, in turn, a preliminary filtration to remove fly ash, treatment with hydrazine to convert bisulfite to sulfite, air-oxidation of the sulfite to sulfate, and ammonolysis of the sulfate in liquid ammonia to yield insoluble ammonium sulfate and an ammonia-hydrazine solution. The ammonium sulfate is separated by centrifugation, and dried by flash evaporation of the ammonia. Anhydrous hydrazine is obtained as a relatively non-volatile liquid by flash evaporation of ammonia, and is returned to the process. However, to the extent that a market exists for anhydrous hydrazine a portion of the product may be sold. In this case make-up hydrazine is supplied either through purchase of dilute hydrazine or through the installation of a small Raschig facility. The Raschig method itself yields anhydrous hydrazine, but for the present purpose only that portion of the overall facility is required which produces 3% aqueous liquor.



Basis :
- 120 megawatt power plant
- 20 million cfh flue gas
- Sale of 34,610 tons SO_2 per year

BASIC ALUMINUM SULFATE PROCESS : PROFITABILITY
Figure 28

An important distinction between this system and the ammonia-based systems is that only one scrubber is used in the Ammonia-Hydrazine process. This change is probably justified because of the relatively low vapor pressure of hydrazine as compared with ammonia; thus, hydrazine stack losses should be negligible.

A flow diagram for the Ammonia-Hydrazine process is shown in Figure 29.

(2) Process Reactions

Scrubber:

$$N_2H_4 + H_2O + SO_2 \longrightarrow N_2H_5HSO_3$$

$$2\,N_2H_4 + H_2O + SO_2 \longrightarrow (N_2H_5)_2SO_3$$

$$(N_2H_5)_2SO_3 + 1/2\ O_2 \longrightarrow (N_2H_5)_2SO_4$$

Mixer:

$$N_2H_5HSO_3 + N_2H_4 \longrightarrow (N_2H_5)_2SO_3$$

Oxidizer:

$$(N_2H_5)_2SO_3 + 1/2\ O_2 \longrightarrow (N_2H_5)_2SO_4$$

Ammoniator:

$$(N_2H_5)_2SO_4 + 2\,NH_3 \xrightarrow{NH_3} (NH_4)_2SO_4 \downarrow + 2\,N_2H_4$$

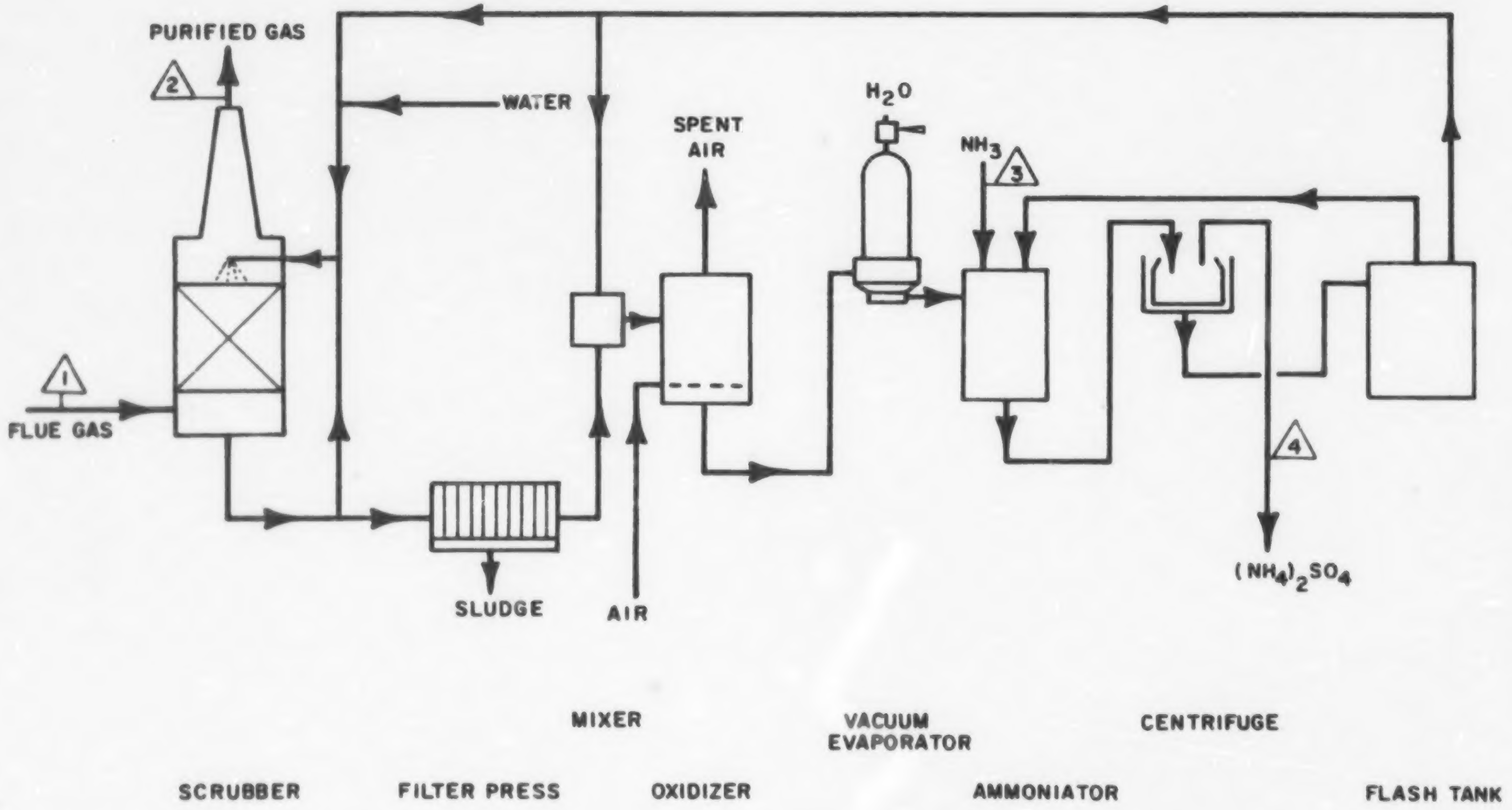
(3) Chemical Requirements and By-Product Yields

As with all of the other processes considered in this study, the reactant chemicals and product yields shown in Figure 29 are theoretical quantities. Due to its low vapor pressure, hydrazine losses should be negligible; as indicated previously, however, ammonia losses experienced in the ammonia-based systems are significant.

The chemical requirements and by-products produced per year for plants of three different sizes are listed in Table 55. It should be noted that the quantity of ammonium sulfate produced is the same as that obtained from a Showa-Denko plant using anhydrous ammonia as the absorbent.

Reactant Chemicals Per Million SCF Flue Gas Processed

△ Stream	Component	Lb Moles	Lbs
1	SO_2	8.36	535
2	SO_2	0.42	26.8
3	NH_3	15.9	270
4	$(NH_4)_2SO_4$	7.94	1048


PURIFIED GAS
2
WATER
SPENT AIR
H₂O
NH₃
3
1
FLUE GAS
4
SLUDGE
AIR
(NH₄)₂SO₄
MIXER
VACUUM EVAPORATOR
CENTRIFUGE
SCRUBBER
FILTER PRESS
OXIDIZER
AMMONIATOR
FLASH TANK

AMMONIA - HYDRAZINE PROCESS : FLOW DIAGRAM

Figure 29

TABLE 55

AMMONIA-HYDRAZINE PROCESS:

CHEMICAL REQUIREMENTS & BY-PRODUCT YIELDS

	Quantity per Million SCF Flue Gas		Tons per Year		
	Lb Mole	Lb	20 Million SCFH Flue Gas	0.5 Million SCFM Flue Gas	2.5 Million SCFM Flue Gas
Raw Materials					
SO_2 (flue gas)	7.94	508	40,230	60,350	301,730
NH_3	15.88	270	21,380	32,070	160,350
By-Product					
$(NH_4)_2SO_4$	7.94	1048	83,000	124,500	622,500

(4) Cost Estimates

(a) Capital Costs

The capital cost of the Showa-Denko process was used as the basis for this system. One of the Showa-Denko scrubber subsystems, including pumps and blower, was eliminated from the present system, resulting in a cost reduction of $240,300. The $35,000 dryer used in the Showa-Denko process was also eliminated. The combined cost of the ammoniator and flash tank which had to be incorporated into the system (see Table 9) were estimated to be $35,000. Thus, the purchased equipment cost for the Ammonia-Hydrazine process is $965,300, as compared with $1,205,600 for the Showa-Denko process. The capital costs are summarized in Table 56.

(b) Operating Costs

A summary of the operating-cost estimate is shown in Table 57. The total operating cost is $2,765,900, or $5.82/ton of coal and 2.91 mill/kwh.

Raw material consumption is based on the quantities shown in Table 55. In-plant losses and hydrazine make-up have not been included in raw material usage.

Four men per shift were considered adequate to operate the plant; a supervision requirement of one foreman per shift and one area superintendent was assumed.

The only significant reduction, other than that created by the lower capital costs, is the lower power requirement which is reduced by 3,550,000 kwh per year due to elimination of the blower and pumps.

(c) Profitability

Figure 30 shows the profitability of the system assuming sale of all of the ammonium sulfate produced (83,000 tons per year). The data indicated a cost of $3-3.50/ton of coal if the ammonium sulfate were sold at one-half the current selling price.

TABLE 56

AMMONIA HYDRAZINE PROCESS: CAPITAL COST ESTIMATE SUMMARY

	ITEM	FACTOR	COST - $
1.	Purchased Equipment	1.00	965,300
2.	Erection Labor	0.25	241,300
3.	Foundation & Platforms	0.18	173,800
4.	Piping	0.76	733,600
5.	Instruments	0.15	144,800
6.	Insulation	0.08	77,200
7.	Electrical	0.10	96,500
8.	Buildings	0.25	241,300
9.	Land & Yard Improvements	0.13	125,600
10.	Utilities	0.40	386,100
11.	Physical-Plant Cost	3.30	3,185,500
12.	Engineering & Construction	0.66	637,100
13.	Direct Plant Cost	3.96	3,822,600
14.	Contractor's Fee	0.19	183,400
15.	Contingency	0.59	569,500
16.	Fixed Capital Cost	4.74	4,575,500
17.	Working Capital, 10%	0.47	453,700
	Total Investment	5.21	5,029,200

18. Capital Requirements
$/kw capacity 41.91

TABLE 57

AMMONIA-HYDRAZINE PROCESS: OPERATING COST ESTIMATE SUMMARY

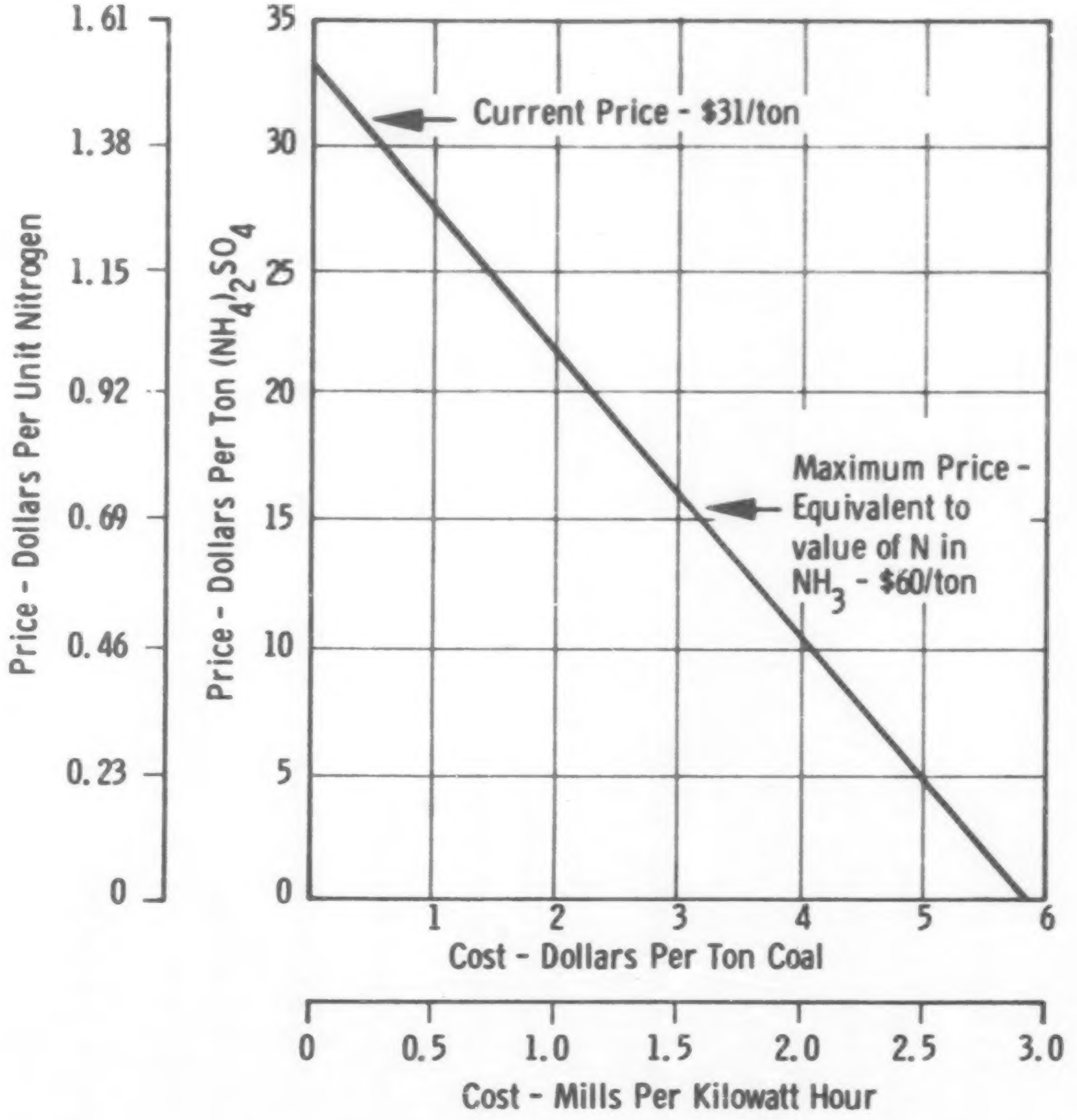
Fixed Capital Cost: $4,575,500

	ITEM	TOTAL $	%
1.	Raw Materials & Chemicals	1,283,000	46.39
2.	Direct Labor	96,000	3.47
3.	Supervision	43,200	1.56
4.	Maintenance, 5% of Fixed Capital	228,800	8.27
5.	Supplies, 15% of Maintenance	34,300	1.24
6.	Utilities	256,700	9.28
7.	Other	-	-
8.	TOTAL DIRECT COST	1,942,000	70.21
9.	Payroll Burden, 20% of 2 & 3	27,800	1.01
10.	Plant Overhead, 50% of 2, 3, 4 & 5	201,200	7.27
11.	Pack & Ship	-	-
12.	Waste Disposal	-	-
13.	Other	-	-
14.	TOTAL INDIRECT COST	229,000	8.28
15.	Depreciation, 10 % Fixed Capital/Yr	457,600	16.54
16.	Taxes, 2% of Fixed Capital	91,500	3.31
17.	Insurance, 1% of Fixed Capital	45,800	1.66
18.	Other	-	-
19.	TOTAL FIXED COST	594,900	21.51
20.	TOTAL OPERATING COST	2,765,900	100.00

21. COST: $/Ton of Coal 5.82

22. Mill/kwh 2.91

23. BY-PRODUCT CREDIT (SEE FIGURE 30)



Basis:
120 megawatt power plant
20 million cfh flue gas
Sale of 83,000 tons $(NH_4)_2SO_4$
per year

AMMONIA-HYDRAZINE PROCESS: PROFITABILITY

Figure 30

q. Ammonia-Hydrazine Exorption Process

(1) Process Description

The Ammonia-Hydrazine Exorption process bears the same relation to the Ammonia-Hydrazine process as does the Cominco Exorption process to the Cominco process. Since the latter three processes have already been discussed, no process description of the Ammonia-Hydrazine Exorption process is considered necessary. A flow diagram of the system is shown in Figure 31.

A variation of the Ammonia-Hydrazine Exorption process, in which the salable produce is monohydrazine sulfate, rather than anhydrous hydrazine and ammonium sulfate, was also considered. However, this process has the disadvantage that monohydrazine sulfate, in contrast to hydrazine, cannot be returned to the process if the amount produced exceeds the demand. Further analysis showed that a single power plant producing 2.5 million SCFM of flue gas would yield more of the sulfate than the equivalent amount of hydrazine consumed in non-military uses in this country in the year 1964. On this basis the process variation was eliminated from further consideration.

(2) Process Reactions

Scrubber:

$$N_2H_4 + SO_2 + H_2O \longrightarrow N_2H_5HSO_3$$

$$2\,N_2H_4 + SO_2 + H_2O \longrightarrow (N_2H_5)_2SO_3$$

$$(N_2H_5)_2SO_3 + 1/2\ O_2 \longrightarrow (N_2H_5)_2SO_4$$

Heater:

$$2\,N_2H_5HSO_3 \longrightarrow (N_2H_5)_2SO_3 + SO_2 \uparrow + H_2O$$

Ammoniator:

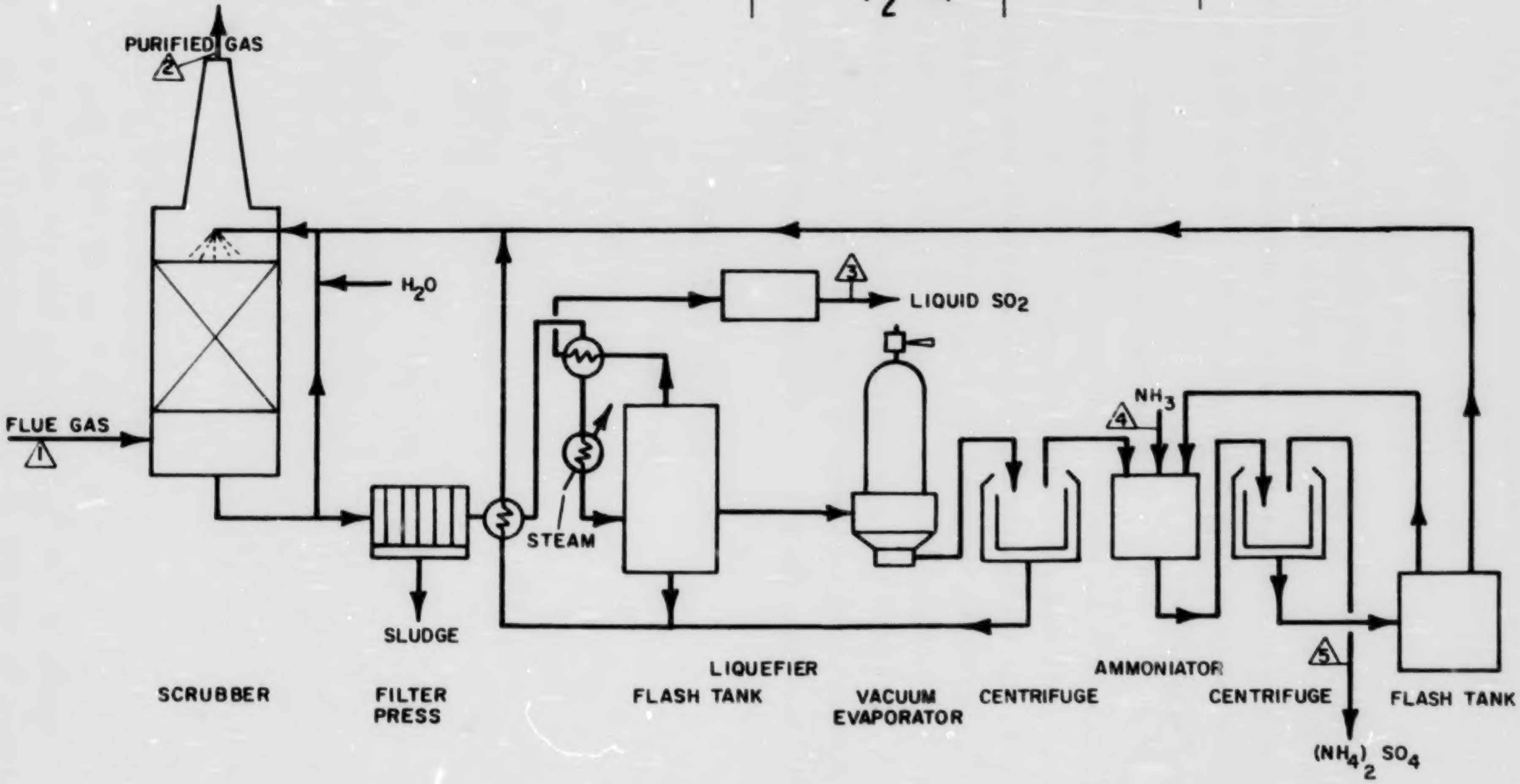
$$(N_2H_5)_2SO_4 + 2\,NH_3 \longrightarrow (NH_4)_2SO_4 + 2\,N_2H_4$$

(3) Chemical Requirements and By-Product Yields

Table 58 lists the theoretical raw material requirements and by-product yields. Reduction of the anhydrous ammonia requirement is the major feature of this process when compared with the Ammonia-Hydrazine process discussed previously.

Reactant Chemicals Per Million SCF Flue Gas Processed

△Stream	Component	Lb Moles	Lbs
1	SO_2	8.36	535
2	SO_2	0.42	26.8
3	SO_2	6.83	437
4	NH_3	2.22	38.0
5	$(NH_4)_2SO_4$	1.11	146


PURIFIED GAS
2
FLUE GAS
1
H₂O
3
LIQUID SO₂
4
NH₃
STEAM
SLUDGE
5
(NH₄)₂ SO₄
SCRUBBER
FILTER PRESS
LIQUEFIER
FLASH TANK
VACUUM EVAPORATOR
CENTRIFUGE
AMMONIATOR
CENTRIFUGE
FLASH TANK

AMMONIA - HYDRAZINE EXORPTION PROCESS : FLOW DIAGRAM

Figure 31

TABLE 58

AMMONIA-HYDRAZINE EXORPTION PROCESS: CHEMICAL REQUIREMENTS & BY-PRODUCT YIELDS

	Quantity per Million SCF Flue Gas		Tons per Year		
	Lb Mole	Lb	20 Million SCFH Flue Gas	0.5 Million SCFM Flue Gas	2.5 Million SCFM Flue Gas
Raw Materials[a]					
SO_2 (flue gas)	7.94	508	40,230	60,350	301,730
NH_3	2.22	38	3,010	4,520	22,580
By-Products					
$(NH_4)_2SO_4$	1.11	147	11,640	17,460	87,300
SO_2	6.83	437	34,610	51,960	259,800

---

[a] Assumes 14% of SO_2 is oxidized to SO_3.

(4) Cost Estimate

The estimate for the Ammonia-Hydrazine Exorption process will be derived from data available in the estimate for the Cominco Exorption process.

(a) Capital Costs

The following items, included in the Cominco Exorption process, can be eliminated:

One scrubbing tower, pumps and blower	-	$240,300
Cooler in scrubber absorbent circulating line	-	53,500
Net change:	-	$293,800

This results in a total investment of $6,155,600, or $51.30/kw capacity. The capital cost is summarized in Table 59.

(b) Operating Costs

The total operating cost is $2,393,200, or $5.04/ton of coal and 2.57 mill/kwh. See Table 60. Raw material costs were derived from the quantities shown in Table 58.

Direct labor has been estimated at 5 men per shift. A supervision requirement of one man per shift and an area supervisor is considered adequate.

Utilities costs will be the same as in the Cominco Exorption process, $756,400 minus a $32,200 reduction in the cooling water requirement.

(c) Profitability

Two by-products are produced in this process: liquid sulfur dioxide and ammonium sulfate. As in the case of the Ammonia-Hydrazine process, anhydrous hydrazine could be produced for sale if desired, depending on the existing hydrazine market.

Figure 32 provides a range of operating costs (and profits) dependent upon the prices assigned to ammonium sulfate and liquid sulfur dioxide. A price range of from zero to current market price is assigned to the two by-products.

TABLE 59

AMMONIA-HYDRAZINE EXORPTION PROCESS: CAPITAL COST ESTIMATE SUMMARY

	ITEM	FACTOR	COST - $
1.	Purchased Equipment	1.00	1,181,500
2.	Erection Labor	0.25	295,400
3.	Foundation & Platforms	0.18	212,700
4.	Piping	0.76	897,900
5.	Instruments	0.15	177,200
6.	Insulation	0.08	94,500
7.	Electrical	0.10	118,200
8.	Buildings	0.25	295,400
9.	Land & Yard Improvements	0.13	153,600
10.	Utilities	0.40	472,600
11.	PHYSICAL-PLANT COST	3.30	3,899,000
12.	Engineering & Construction	0.66	779,700
13.	DIRECT PLANT COST	3.96	4,678,700
14.	Contractor's Fee	0.19	224,500
15.	Contingency	0.59	697,100
16.	FIXED CAPITAL COST	4.74	5,600,300
17.	Working Capital, 10%	0.47	555,300
	TOTAL INVESTMENT	5.21	6,155,600

18. **Capital Requirements**

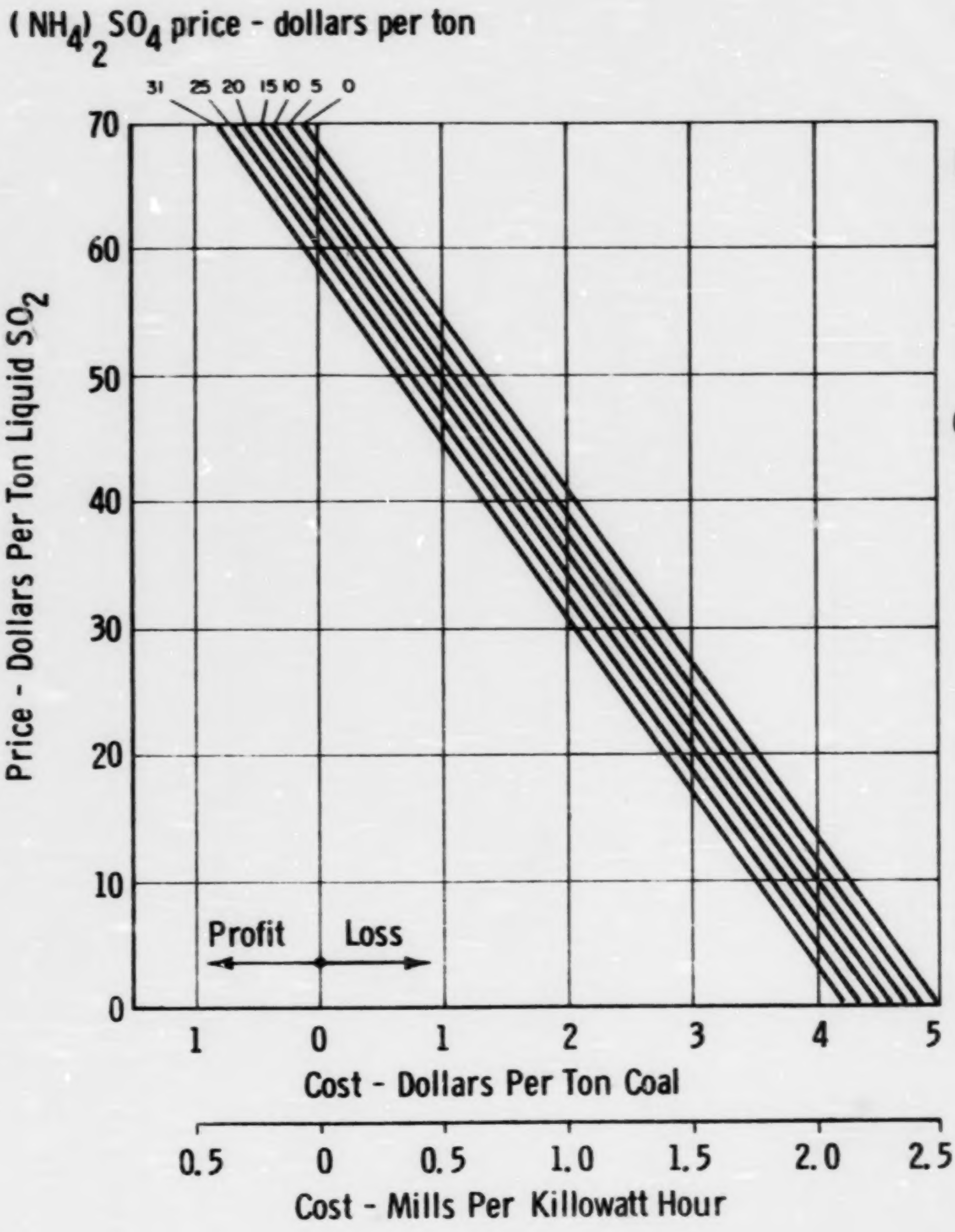
$/kw capacity 51.30

TABLE 60

AMMONIA-HYDRAZINE EXORPTION PROCESS: OPERATING COST ESTIMATE SUMMARY

Fixed Capital Cost: $5,600,300

	ITEM	TOTAL $	%
1.	**Raw Materials & Chemicals**	180,600	7.55
2.	**Direct Labor**	120,000	5.01
3.	**Supervision**	43,200	1.81
4.	**Maintenance, 5% of Fixed Capital**	280,000	11.70
5.	**Supplies, 15% of Maintenance**	42,000	1.75
6.	**Utilities**	724,200	30.26
7.	**Other**	-	-
8.	**TOTAL DIRECT COST**	1,390,000	58.08
9.	**Payroll Burden, 20% of 2 & 3**	32,600	1.36
10.	**Plant Overhead, 50% of 2, 3, 4 & 5**	242,600	10.14
11.	**Pack & Ship**	-	-
12.	**Waste Disposal**	-	-
13.	**Other**	-	-
14.	**TOTAL INDIRECT COST**	275,200	11.50
15.	**Depreciation, 10 % Fixed Capital/Yr**	560,000	23.40
16.	**Taxes, 2% of Fixed Capital**	112,000	4.68
17.	**Insurance, 1% of Fixed Capital**	56,000	2.34
18.	**Other**	-	-
19.	**TOTAL FIXED COST**	728,000	30.42
20.	**TOTAL OPERATING COST**	2,393,200	100.00
21.	**COST: $/Ton of Coal** 5.04		
22.	**Mill/kwh** 2.57		
23.	**BY-PRODUCT CREDIT**	(SEE FIGURE 32)	



Basis :
- 120 megawatt power plant
- 20 million cfh flue gas
- Sale of 11,640 tons $(NH_4)_2SO_4$ and 34,610 tons SO_2 per year

Current Prices :
- Liquid SO_2 : \$69/ton
- $(NH_4)_2SO_4$: \$31/ton

AMMONIA - HYDRAZINE - EXORPTION PROCESS : PROFITABILITY

Figure 32

r. Mitsubishi Ammoniacal Liquor Process

(1) Process Description

The Mitsubishi Ammoniacal Liquor process[15] is markedly similar to the Showa-Denko process, and for this reason a separate flow diagram for the process was not prepared. The two processes differ in that the Mitsubishi process the first gas scrubber contains a more highly concentrated ammonium sulfite-bisulfite solution, so that a vacuum evaporator for workup of the off-stream liquor is no longer required. By cooling the liquid effluent from the first scrubber before entry into the second scrubber, the ammonia losses were reduced to 0.2% of the makeup ammonia. The ammonia is not injected into the flue gas stream as in the Showa-Denko process, but is added directly to the scrubber liquor.

(2) Process Reactions

Scrubber:

$$NH_3 + H_2O + SO_2 \longrightarrow NH_4HSO_3$$

$$2\,NH_3 + H_2O + SO_2 \longrightarrow (NH_4)_2SO_3$$

$$(NH_4)_2SO_3 + 1/2\ O_2 \longrightarrow (NH_4)_2SO_4$$

Mixer:

$$NH_4HSO_3 + NH_3 \longrightarrow (NH_4)_2SO_3$$

Oxidizer:

$$(NH_4)_2SO_3 + 1/2\ O_2 \longrightarrow (NH_4)_2SO_4$$

(3) Chemical Requirements and By-Product Yields

The chemical requirements and by-product yields are the same as those shown in connection with the Showa-Denko process (see Table 8).

(4) Cost Estimate

The Showa-Denko process was utilized as the basis for a cost estimate for the Mitsubishi process.

(a) Capital Costs

The purchased equipment cost in this system would be slightly less than in the Showa-Denko process due to the following changes:

Eliminate evaporator	-\$121,000
Add cooler	+ 96,000
Net change:	- \$25,000

This change results in a fixed capital charge of \$6,139,200 and a total investment of \$6,150,900, or a cost of \$51.26 per kilowatt.

(b) Operating Costs

The operating cost would increase slightly over the Showa-Denko system, as follows:

Lower steam requirements due to elimination of evaporator	-\$6,000
Increase cooling water	+90,000
Lower fixed costs (less depreciation, insurance, and taxes)	-15,400
Net change:	+\$68,600

The increase in annual operating cost increases the unit cost per ton of coal to \$6.47 with no by-product credits.

(c) Profitability

A profitability chart was not prepared for this system since there is only a slight variation from the Showa-Denko process. The costs per ton of coal are as follows:

No by-product credit	\$6.47
Full credit for $(NH_4)_2SO_4$	\$1.05
$(NH_4)_2SO_4$ credit at \$15.50/ton	\$3.76

s. Mitsubishi Manganese Oxyhydroxide Process

(1) Process Description

In the Mitsubishi Manganese Oxyhydroxide process, a 3 percent slurry of manganese oxyhydroxide is utilized for the absorption of sulfur dioxide.[15] A portion of the absorbing slurry is continually withdrawn and treated with ammonia and air in order to regenerate the manganese oxyhydroxide, which is then returned to the scrubber. The ammonia is converted to soluble ammonium sulfate, which is removed as a 45 percent solution after clarification. The solution is further concentrated in a crystallizer, and the precipitated crystalline solid is separated by centrifugation and dried. A flow diagram of the Mitsubishi Manganese Oxyhydroxide process is shown in Figure 33.

(2) Process Reactions

Scrubber:

$$4SO_2 + 4\,Mn(OH)O\downarrow + O_2 \longrightarrow 4\,MnSO_4 + 2\,H_2O$$

Mixer-Oxidizer:

$$4\,MnSO_4 + 8\,NH_3 + O_2 \longrightarrow 4\,Mn(OH)O\downarrow + 4\,(NH_4)_2SO_4$$

(3) Cost Estimate

Very few data for this process were found in the literature. The flow diagram shows our conception of the system. The data provided in the Bureau of Mines study[621] again was used for estimating purposes.

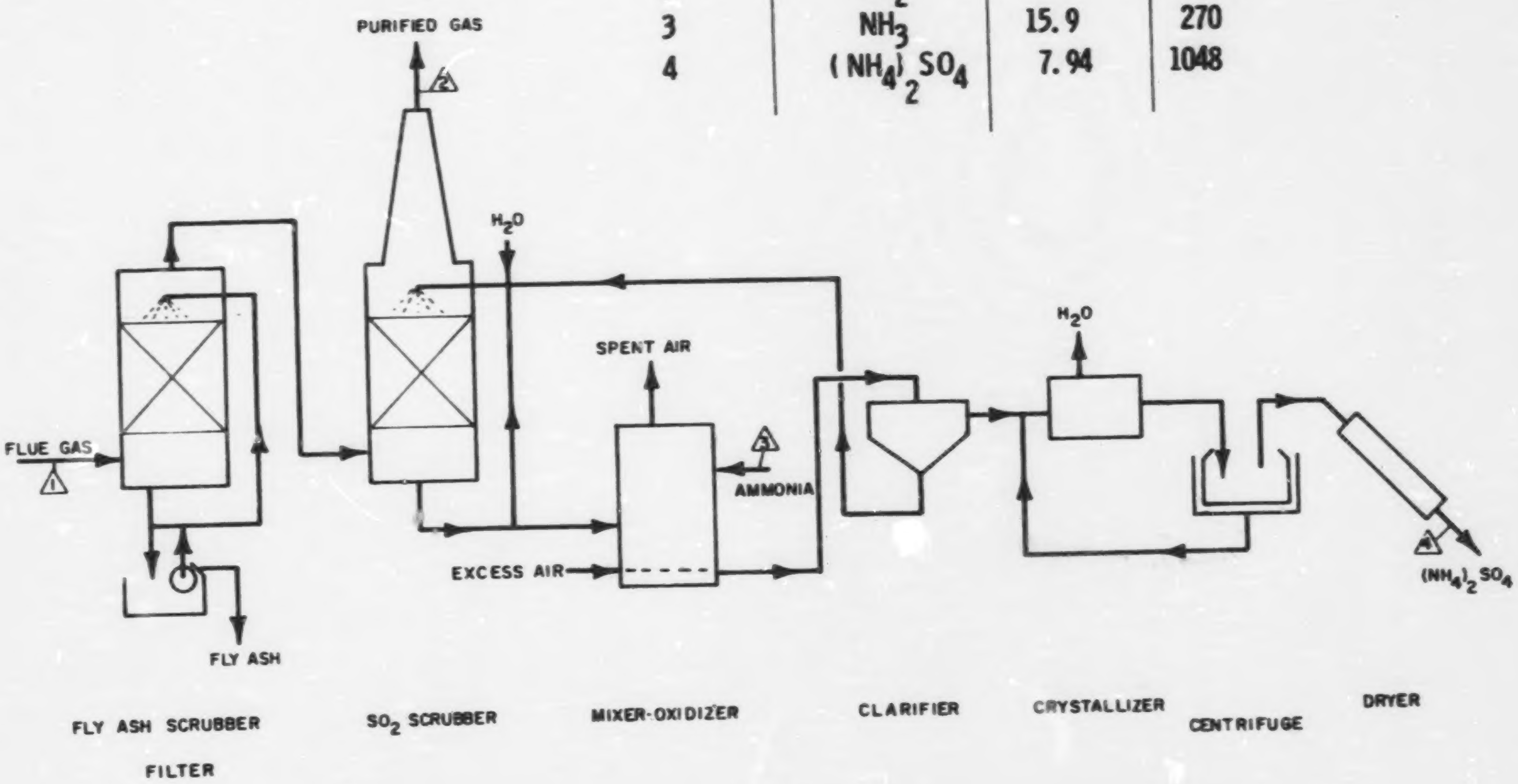
(a) Capital Costs

The fly ash scrubber subsystem is similar to the one used as the main SO_2 scrubber in the Zinc Oxide process. The purchased equipment cost is $215, 600. The filter press was also selected from the same system; purchased cost is $84. 800.

In the Howden-I. C. I. system lime or chalk slurry is used for removing SO_2 from flue gases. Since a slurry scrubbing medium is also used in the present process, the Howden-I. C. I. scrubber was considered suitable. The purchased cost of this unit is $263, 600.

Reactant Chemicals Per Million SCF Flue Gas Processed

△Stream	Component	Lb Moles	Lbs
1	SO_2	8.36	535
2	SO_2	0.42	26.9
3	NH_3	15.9	270
4	$(NH_4)_2SO_4$	7.94	1048


PURIFIED GAS
2
H₂O
SPENT AIR
H₂O
FLUE GAS
1
3
AMMONIA
EXCESS AIR
4
(NH₄)₂ SO₄
FLY ASH
FLY ASH SCRUBBER
FILTER
SO₂ SCRUBBER
MIXER-OXIDIZER
CLARIFIER
CRYSTALLIZER
CENTRIFUGE
DRYER

MITSUBISHI MANGANESE OXYHYDROXIDE PROCESS : FLOW DIAGRAM

Figure 33

Two 150,000-gal lead-lined steel tanks similar to those specified in the Magnesium Hydroxide process were selected for the air oxidizer and mixer subsystem. The purchased cost, including an air compressor, is $93,400.

The clarifier in the Zinc Oxide system was selected for use in that step in which the magnesium oxyhydroxide is allowed to settle. The purchased cost is $46,800.

A large amount of ammonia is used in this process. A storage system similar to that specified in the Fulham-Simon-Carves process was selected. The equipment required is as follows:

Pressure sphere, 229,000 gal, with refrigerator and compressor	$105,500
Storage tank, 3,935 gal, for 15% NH_3 liquor	7,200
Head tank, 3,935 gal, for 15% NH_3 liquor	7,200
Total:	$119,900

Although an evaporator is not needed in this process,[15] a crystallizer is required. Cost File 133[61] lists complete costs for crystallizer and dryer systems for ammonium sulfate, which include the vacuum system, instrumentation, pumps, centrifugation and drying equipment, insulation and piping. In terms of purchased cost, this amounts to $600 per ton of ammonium sulfate per day. At 250 tons per day, the purchased equipment cost is $150,000.

The cost of various pumps was estimated at $41,400.

The total purchased equipment cost is $1,015,500. The total investment is $5,290,800, or $44.09/kw capacity. See Table 61.

TABLE 61

MITSUBISHI MANGANESE OXYHYDROXIDE PROCESS: CAPITAL COST ESTIMATE SUMMARY

	ITEM	FACTOR	COST - $
1.	Purchased Equipment	1.00	1,015,500
2.	Erection Labor	0.25	253,900
3.	Foundation & Platforms	0.18	182,800
4.	Piping	0.76	771,800
5.	Instruments	0.15	152,300
6.	Insulation	0.08	81,200
7.	Electrical	0.10	101,600
8.	Buildings	0.25	253,900
9.	Land & Yard Improvements	0.13	132,000
10.	Utilities	0.40	406,200
11.	Physical-Plant Cost	3.30	3,351,200
12.	Engineering & Construction	0.66	670,200
13.	Direct Plant Cost	3.96	4,021,400
14.	Contractor's Fee	0.19	192,900
15.	Contingency	0.59	599,200
16.	Fixed Capital Cost	4.74	4,813,500
17.	Working Capital, 10%	0.47	477,300
	Total Investment	5.21	5,290,800

18. Capital Requirements
$/kw capacity 44.09

(b) Operating Costs

The raw material requirements for the Mitsubishi Manganese Oxyhydroxide process are shown in Table 62 and the operating costs in Table 63. The latter totals \$2,849,300, or \$6.00/ton of coal and 3.00 mill/kwh.

Direct labor was estimated at 5 men per shift with one foreman per shift, and one area superintendent.

Since dependable data were not available, the utilities requirements were assumed to be the same as those of a similar process, the Magnesium Hydroxide process.

(c) Profitability

Figure 34 shows the profitability for the Mitsubishi Manganese Oxyhydroxide process. It appeared that the net cost would be \$3-4/ton of coal and 1.5-2.0 mill/kwh.

TABLE 62

MITSUBISHI MANGANESE OXYHYDROXIDE PROCESS: CHEMICAL REQUIREMENTS & BY-PRODUCT YIELDS

	Quantity per Million SCF Flue Gas		Tons per Year		
	Lb Mole	Lb	20 Million SCFH Flue Gas	0.5 Million SCFM Flue Gas	2.5 Million SCFM Flue Gas
Raw Materials					
SO_2 (flue gas)	7.94	508	40,230	60,350	301,730
NH_3	15.88	270	21,380	32,070	160,350
By-Product					
$(NH_4)_2SO_4$	7.94	1048	83,000	124,500	622,500

TABLE 63

MITSUBISHI MANGANESE OXYHYDROXIDE PROCESS: OPERATING COST ESTIMATE SUMMARY

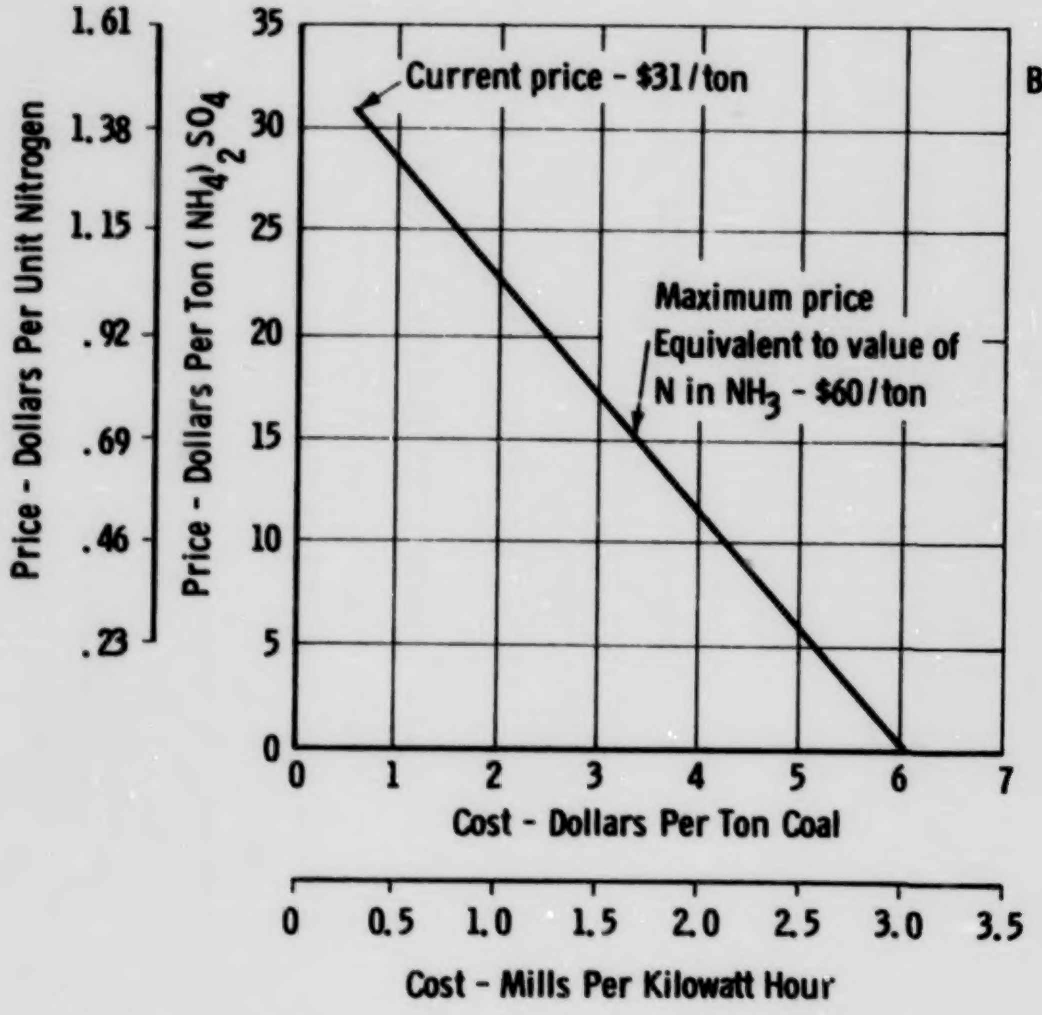
Fixed Capital Cost: $4,813,500

	ITEM	TOTAL $	%
1.	Raw Materials & Chemicals	1,282,800	45.02
2.	Direct Labor	120,000	4.21
3.	Supervision	43,200	1.52
4.	Maintenance, 5% of Fixed Capital	240,700	8.45
5.	Supplies, 15% of Maintenance	36,100	1.27
6.	Utilities	248,100	8.70
7.	Other	-	-
8.	TOTAL DIRECT COST	1,970,900	69.17
9.	Payroll Burden, 20% of 2 & 3	32,600	1.14
10.	Plant Overhead, 50% of 2, 3, 4 & 5	220,000	7.72
11.	Pack & Ship	-	-
12.	Waste Disposal	-	-
13.	Other	-	-
14.	TOTAL INDIRECT COST	252,600	8.86
15.	Depreciation, 10 % Fixed Capital/Yr	481,400	16.90
16.	Taxes, 2% of Fixed Capital	96,300	3.38
17.	Insurance, 1% of Fixed Capital	48,100	1.69
18.	Other	-	-
19.	TOTAL FIXED COST	625,800	21.97
20.	TOTAL OPERATING COST	2,849,300	100.00

21. COST: $/Ton of Coal 6.00

22. Mill/kwh 3.00

23. BY-PRODUCT CREDIT (SEE FIGURE 34)



Basis :
- 120 megawatt power plant
- 20 million cfh flue gas
- Sale of 83,000 tons $(NH_4)_2SO_4$ per year

MITSUBISHI MANGANESE OXYHYDROXIDE PROCESS : PROFITABILITY

Figure 34

t. Mitsubishi Lime Process

(1) Process Description

A 10% lime or limestone slurry is used in the Mitsubishi Lime process as the absorbent for sulfur dioxide. The process is similar to the Howden-I. C. I. (Cyclic Lime) method. The main difference is that calcium sulfate of high purity is obtained in the Mitsubishi method; it will be recalled that the calcium sulfate produced in the Howden process is a highly contaminated, nonsalable material. The high purity of the calcium sulfate product is presumably a consequence of working with a scrubber effluent solution which is free of fly ash.

(2) Process Reactions

Scrubber:

$$SO_2 + Ca(HCO_3)_2 \longrightarrow CaSO_3 \downarrow + 2CO_2 + H_2O$$

$$CaSO_3 + 1/2\ O_2 \longrightarrow CaSO_4 \downarrow$$

Makeup Tank:

$$CaO + CO_2 \longrightarrow CaCO_3 \downarrow$$

and/or

$$CaCO_3 \downarrow + H_2O + CO_2 \rightleftharpoons Ca(HCO_3)_2$$

Oxidizer Tank:

$$CaSO_3 \downarrow + 1/2\ O_2 \longrightarrow CaSO_4 \downarrow$$

(3) Chemical Requirements and Waste Product Yields

Table 64 gives the raw material requirements and the waste products for treating one million SCF of flue gas by the Mitsubishi process. Although the data shown are applicable for the case where lime (calcium oxide) is used, slaked lime (calcium hydroxide) or limestone (calcium carbonate) can be employed.

(4) Cost Estimate

Since this system is similar to the Howden-I. C. I. process, the latter was used as the basis for the cost estimate.

TABLE 64

MITSUBISHI LIME PROCESS:

CHEMICAL REQUIREMENTS & BY-PRODUCT YIELDS FOR THE SYSTEM USING LIME

	Quantity per Million SCF Flue Gas		Tons per Year		
	Lb Mole	Lb	20 Million SCFH Flue Gas	0.5 Million SCFM Flue Gas	2.5 Million SCFM Flue Gas
Raw Materials					
SO_2 (flue gas)	7.94	508	40,235	60,350	301,730
CaO	7.94	445	35,215	52,825	264,115
By-Product					
$CaSO_4$	7.94	1367	108,300	162,450	812,250

(a) Capital Costs

The reference describing the Mitsubishi wet processes states that the equipment cost of the Lime process is about twice that of the Simplified Lime processes.[15] As indicated previously, the Simplified Lime process is considered identical to the Howden-I. C. I. process. On this basis, the capital cost for the Lime process was obtained by doubling the Howden-I. C. I. capital cost, resulting in a fixed capital cost of $4,839,500 and a total investment of $5,319,400. This is equivalent to $44.33 per kw capacity.

(b) Operating Costs

The operating cost summary is shown in Table 65, which shows an annual cost of $1,981,900, or $4.17/ton of coal and 2.09 mill/kwh.

Raw materials charges remain the same as in the Howden-I. C. I. process.

Direct labor was increased from four to five men per shift due to the addition of the drying system.

Utilities charges were increased to handle the additional operations needed to obtain pure calcium sulfate.

Waste disposal costs were eliminated since the process is designed to provide high-purity calcium sulfate.

(c) Profitability

In this process the calcium sulfate is produced as a pure material which can presumably be sold.* Figure 35 shows the profitability of the process applying various credits to this by-product.

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* The Phase III evaluation showed that the market would be limited for this material in the United States.

TABLE 65

MITSUBISHI LIME PROCESS: OPERATING COST ESTIMATE SUMMARY

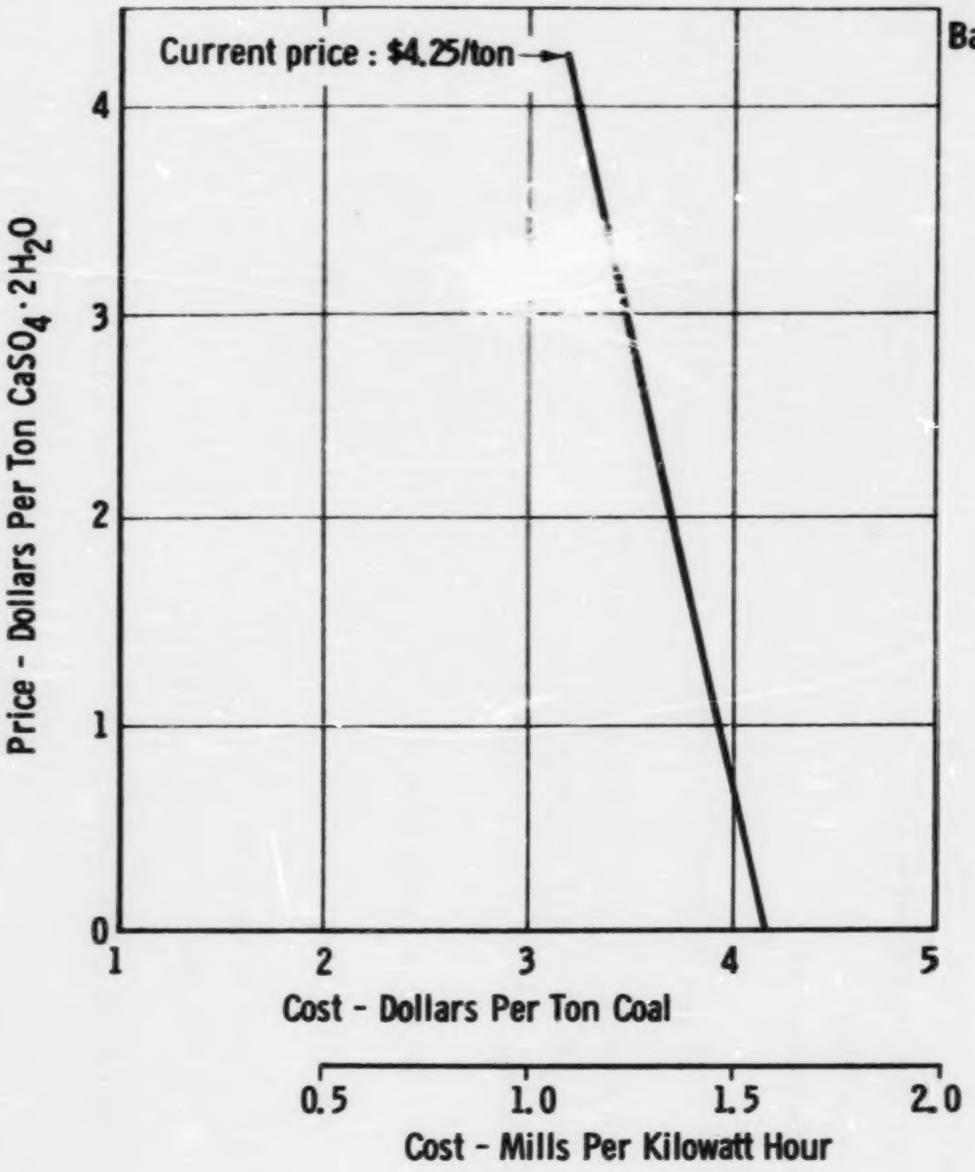
Fixed Capital Cost: $4,839,500

	ITEM	TOTAL $	%
1.	Raw Materials & Chemicals	545,800	27.54
2.	Direct Labor	120,000	6.06
3.	Supervision	43,200	2.18
4.	Maintenance, 5% of Fixed Capital	242,000	12.21
5.	Supplies, 15% of Maintenance	36,300	1.83
6.	Utilities	112,000	5.65
7.	Other	-	-
8.	TOTAL DIRECT COST	1,099,300	55.47
9.	Payroll Burden, 20% of 2 & 3	32,600	1.64
10.	Plant Overhead, 50% of 2, 3, 4 & 5	220,800	11.14
11.	Pack & Ship	-	-
12.	Waste Disposal	-	-
13.	Other	-	-
14.	TOTAL INDIRECT COST	253,400	12.78
15.	Depreciation, 10 % Fixed Capital/Yr	484,000	24.42
16.	Taxes, 2% of Fixed Capital	96,800	4.88
17.	Insurance, 1% of Fixed Capital	48,400	2.44
18.	Other	-	-
19.	TOTAL FIXED COST	629,200	31.75
20.	TOTAL OPERATING COST	1,981,900	100.00

21. COST: $/Ton of Coal 4.17

22. Mill/kwh 2.09

23. BY-PRODUCT CREDIT (SEE FIGURE 35)



Basis :
- 120 megawatt power plant
- 20 million cfh flue gas
- Sale of 108,300 tons $CaSO_4 \cdot 2H_2O$ per year

MITSUBISHI LIME PROCESS : PROFITABILITY

Figure 35

u. Mitsubishi Red Mud Process

(1) Process Description

The absorbent used in the Mitsubishi Red Mud process[15] is a slurry of red mud, the residue resulting from the extraction of alumina from bauxite. In the simplest application of this method, the scrubber effluent is discarded after sulfur dioxide absorption. This is the approach on which the present analysis is based. In another version of this process, one for which very little information is available, the solid residue remaining after absorption is separated into the fractions which are rich in alumina, silica, and ferric oxide, respectively. These are utilized as industrial materials.

(2) Process Reactions

The component in red mud which reacts with SO_2 may be considered to be sodium oxide.

Scrubber:

$$Na_2O + SO_2 \longrightarrow Na_2SO_3$$

$$Na_2SO_3 + 1/2\ O_2 \longrightarrow Na_2SO_4$$

(3) Chemical Requirements and By-Product Yields

Table 66 gives the raw material requirements and waste-product yields for the process. The waste products are shown as dry weights; in addition, it was assumed that approximately 35% free water will be included in the total weight.

(4) Cost Estimate

Due to the very limited data on the Red Mud process, the estimate was made only on the basis of a once-through operation, i.e., the spent red mud is simply discarded after use.

(a) Capital Costs

It was assumed that the Howden-I. C. I. process equipment could be adapted to this system. Accordingly, the same fixed capital

TABLE 66

MITSUBISHI RED MUD PROCESS:
CHEMICAL REQUIREMENTS & BY-PRODUCT YIELDS

	Quantity per Million SCF Flue Gas		Tons per Year		
	Lb Mole	Lb	20 Million SCFH Flue Gas	0.5 Million SCFM Flue Gas	2.5 Million SCFM Flue Gas
Raw Materials					
SO_2 (flue gas)	7.94	508	40,230	60,350	301,730
Red Mud (dry)	7.94[a]	~6000[b]	475,200	712,800	3,564,000
By-Product					
Red Mud Slurry containing reacted SO_2	-	6508	515,430	773,150	3,865,730

---

[a] Equivalent to active ingredient, Na_2O, which accounts for 8.3% of total weight.

[b] Total dry weight.

cost of $2,419,800, or a capital requirement of $22.16 per kilowatt capacity, was assigned to the Red Mud process.

(b) Operating Costs

Where applicable, the various cost elements of the Howden-I.C.I. process were used.

It was assumed that a plant using red mud slurry for removal of SO_2 from flue gas would be located near the bauxite processing facility. No charge was made for acquisition of the raw material.

The waste disposal costs are very high due to the quantity of waste products which have to be handled.

Table 67 summarizes these costs. The $7.58 per ton of coal operating cost would be reduced to $1.72 per ton if there was no cost associated with waste disposal (this assumes that the adjacent bauxite plant which generated the red mud has suitable disposal facilities on-site).

(c) Profitability

The profitability of this system is not indicated in graphical form. Its application as a process is limited by the availability of red mud since one 1400 megawatt power plant (Case III) would generate enough SO_2 to consume approximately all of the red mud available in the United States. It is doubtful that the process would be economical if disposal of waste products represents a substantial cost. Adequate data were not available to evaluate conversion of these waste products into salable industrial materials.

TABLE 67

MITSUBISHI RED MUD PROCESS: OPERATING COST ESTIMATE SUMMARY

Fixed Capital Cost: $2,419,000

	ITEM		TOTAL $	%
1.	Raw Materials & Chemicals		-0-	-
2.	Direct Labor		96,000	2.67
3.	Supervision		43,200	1.20
4.	Maintenance, 5% of Fixed Capital		121,000	3.36
5.	Supplies, 15% of Maintenance		18,200	0.51
6.	Utilities		56,200	1.56
7.	Other		-	-
8.	TOTAL DIRECT COST		334,600	9.30
9.	Payroll Burden, 20% of 2 & 3		27,800	0.77
10.	Plant Overhead, 50% of 2, 3, 4 & 5		139,200	3.87
11.	Pack & Ship		-	-
12.	Waste Disposal		2,783,300	77.32
13.	Other		-	-
14.	TOTAL INDIRECT COST		2,950,300	81.96
15.	Depreciation, 10 % Fixed Capital/Yr		242,000	6.72
16.	Taxes, 2% of Fixed Capital		48,400	1.35
17.	Insurance, 1% of Fixed Capital		24,200	0.67
18.	Other		-	-
19.	TOTAL FIXED COST		314,600	8.74
20.	TOTAL OPERATING COST		3,599,500	100.00
21.	COST: $/Ton of Coal	7.58		
22.	Mill/kwh	3.79		
23.	BY-PRODUCT CREDIT		NONE	

v. Other Processes

Several of the processes listed in Table 1 were evaluated as part of the Phase I effort. Many of these are under current development in this country and are, in large part, proprietary, so that available data are not sufficient to permit a meaningful analysis. For such processes, only the individual contractors involved in the development of these processes can adequately provide economic analyses of the type considered in the preceding sections of the report.

By mutual agreement with NAPCA for the present program, the evaluation of the following processes was considered to lie beyond the scope of the present effort:

- Wisconsin Electric Power
- Wisconsin Electric Power/Universal Oil Products
- Combustion Engineering
- Bechtel
- Ionics/Stone and Webster

Some information was supplied by NAPCA relating to the Wellman Lord/Beckwell process, and an evaluation was planned for this process. However, a large portion of the process data were undisclosed in the literature provided, and it was finally concluded that a meaningful analysis could not be carried out. A Belgian patent,[569] which became available at a later date, provided a general description of the process. Potassium sulfite in an aqueous system is used as the absorbent to remove the SO_2 from the flue gas. Three major operations are used in the process: reactor, crystallization, and stripping. In the first step, a part of the excess potassium sulfite and the SO_2 react with the formation of potassium bisulfite. In the second operation, the solution is cooled resulting in the transformation of potassium bisulfite to potassium pyrosulfite during crystallization. After filtration the crystals of potassium pyrosulfite are heated in the third operation yielding potassium sulfite and SO_2. The potassium sulfite is returned to the reactor operation while the SO_2 is recovered as liquid SO_2 or as sulfur. The crystallization of potassium pyrosulfite and its conversion to potassium sulfite and SO_2 apparently are the main economic advantages of the process. Potassium sulfate formed, due to the presence of SO_3, has to be removed periodically. In addition, the potassium sulfite may react with the oxygen in the flue gas to yield more potassium sulfate. It may be necessary, therefore, to use oxidation inhibitors such as hydroquinone to prevent this reaction. A laboratory program comparing the behavior of potassium and sodium ions as absorbents was of interest and is reported in Volume II of this Final Report.

Of the entries in Table 1 only the Kanagawa, Guggenheim, and Diethylenetriamine processes remain to be discussed. Of these the Kanagawa process could not be evaluated because of the sparcity of available data. However, it was evident from the single reference available on this process[62] that the scrubber medium is a naturally occurring water, and consequently it will exhibt a low capacity for SO_2. On this basis, the process may be compared with the Haenisch-Schroeder, Battersea, and other processes involving a water scrubber and, as will be seen in a subsequent section of the report dealing with process selection (Section II, C, 3), this type of process is among the poorest candidates for a continuing effort in Phase III of the present program. In particular, the capital cost of all such processes is exorbitant, because of the large scrubbing towers needed to offset the low absorbing capacity of the scrubber medium.

The Guggenheim process was not evaluated because it differs substantially from the Cominco Exorption process only in that in the former process recovered SO_2 is reduced to elemental sulfur by heating with coke. This step is applicable in general whenever SO_2 appears as a product, and the conversion of SO_2 to other salable forms of sulfur, including elemental sulfur, will be treated as a separate section of this report (see Section III. C. 3. e).

Aqueous solutions of various aliphatic amines have been proposed from time to time as substitutes for aqueous ammonia in the Cominco Exorption process. The main advantage of an amine over ammonia is its relative non-volatility, so that during the thermal regeneration of SO_2 little or no amine is lost, and the regeneration step can be carried to any desired degree of completion, limited only by the cost of steam. Diethylenetriamine is one example of a proposed amine. The Diethylenetriamine process was not fully evaluated on the current program because only initial laboratory studies had been reported, so that very few data were available on which to base an economic analysis. The following remarks, however, are relevant to this process in particular, and to the use of amines in general.

Aliphatic amines are more basic than ammonia ($K_B = 1.8 \times 10^{-5}$) so that absorbed SO_2 is more tightly held. This situation is unfavorable to thermal regeneration and, in fact, Johnstone[224] has indicated that for overall minimum steam requirements the absorbing amine should exhibit a base constant of about 10^{-8}. Another general limitation to the use of amines is the limited solubility of amine sulfites in water relative to that of ammonium sulfite. This is particularly true of amines containing a relatively high C/N ratio, in which case the effect is a decrease in the capacity of the absorbing solution.

The polyethylene amines, of general formula $H_2N(CH_2CH_2NH)_xCH_2CH_2NH_2$, where $x \leq 4$, contain secondary amine functions whenever $x > 1$. In general, secondary amines exhibit larger base constants than primary amines, so that if $x > 1$ the polyamine should be more basic than ethylenediamine ($x = 1$, $K_B = 8.5 \times 10^{-5}$).

The ethanolamines, $H_xN(CH_2CH_2OH)_y$, where $x > 0$ and $x - y = 3$, were found by Johnstone to be readily oxidized in experiments involving SO_2 absorption, even in the absence of air, and thus appear to be eliminated as scrubber components on this basis alone.

3. Process Selection

a. Introduction

A comparative economic analysis of the processes in this study was needed in order to select candidates for Phase III. Several important factors which affected this assessment include:

- Total capital investment and investment per kilowatt of generating capacity (see Figure 36).
- Operating cost expressed as dollars per ton of coal consumed or as mills per kilowatt hour (see Figure 37).
- By-product utilization and/or disposal, and justification of credits applied to operating cost.
- The impact of the by-product on the economy of the United States.

Figure 36

COMPARATIVE ASSESSMENT OF AQUEOUS BASED PROCESSES FOR REMOVING SO_2 FROM FLUE GASES
——CAPITAL INVESTMENT——

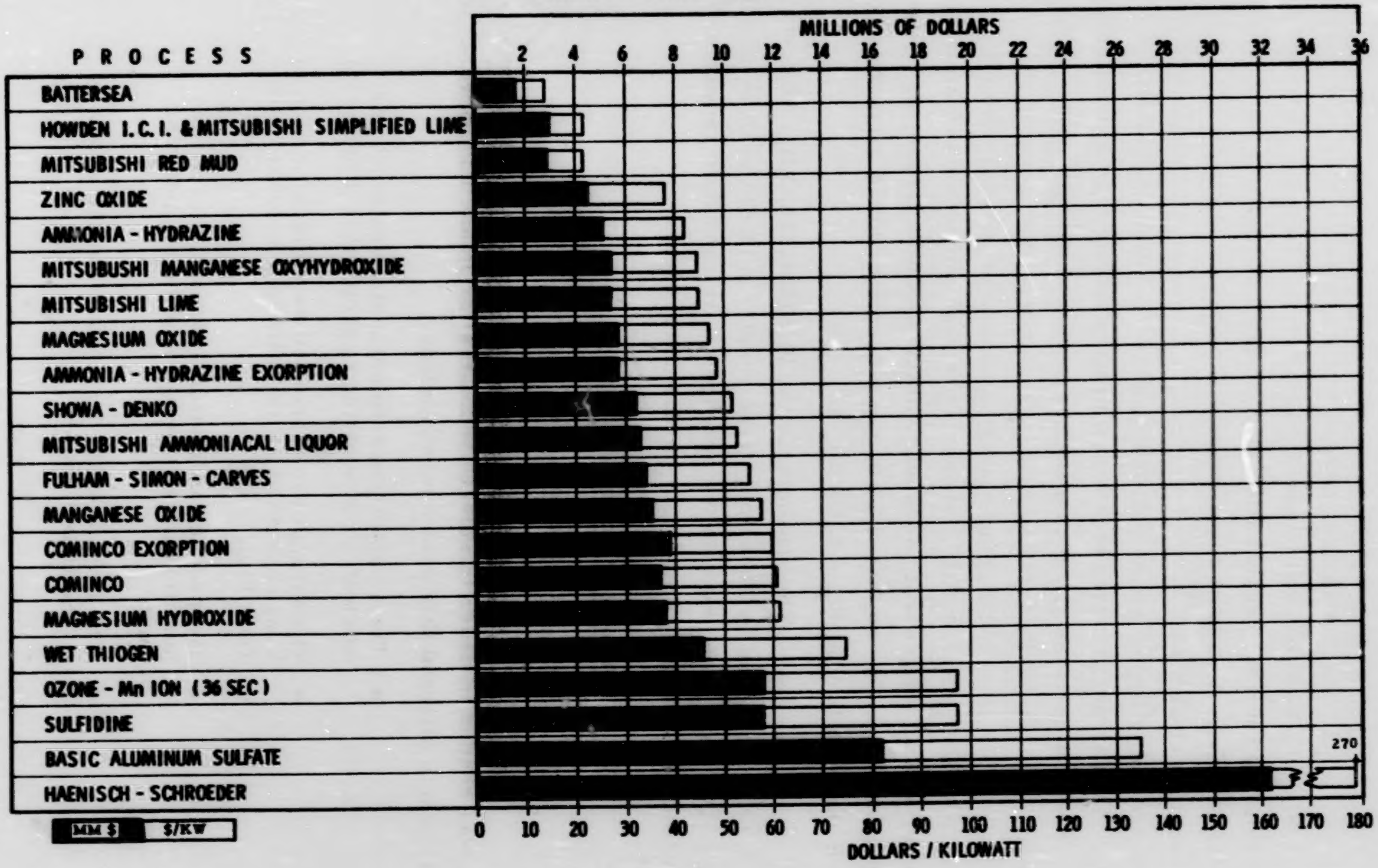
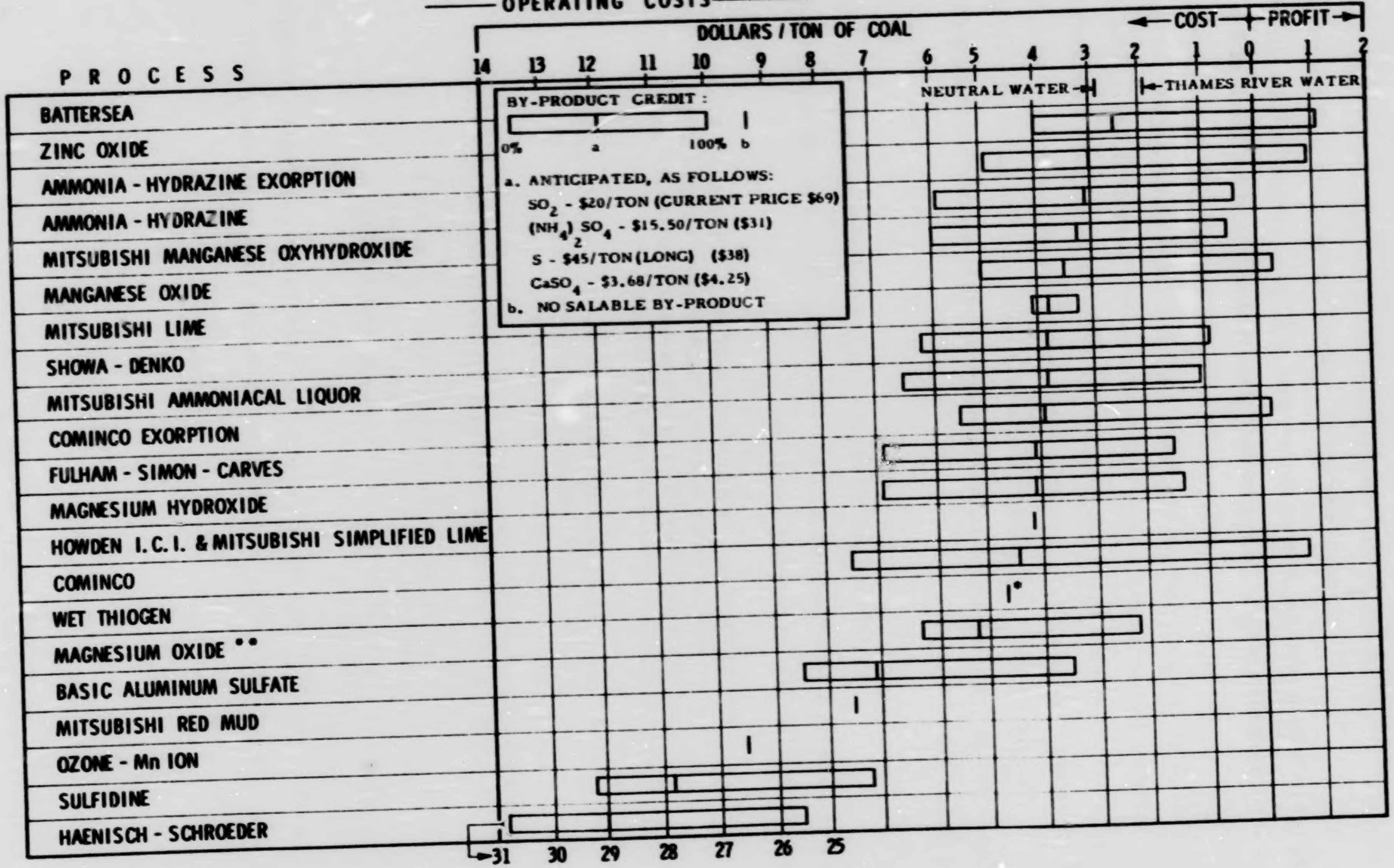


Figure 37

COMPARATIVE ASSESSMENT OF AQUEOUS BASED PROCESSES FOR REMOVING SO_2 FROM FLUE GASES

OPERATING COSTS



* By-product sulfur fully credited

** Assumes 28% oxidation of removed, SO_2 to $MgSO_4$ which for purposes of this comparative analysis would be discarded. 10% oxidation was assumed for most other processes listed.

Consideration of capital investment and operating costs in this analysis was based on comparative and not on absolute values due to the nature of the cost estimates used. By-product generation could be analyzed in a more absolute fashion since the annual quantity of SO_2 emissions from power plants was easily related to the amounts of the various by-products obtained. The value applied to these by-products, as mentioned before, was critical. The range of by-product credit shown for each process in Figure 37 included extreme cases in which either no credit or full credit was allowed, based on prices which were current in February 1968. Neither of these cases was considered realistic. Within this range was included an anticipated credit, based on anticipated by-product selling prices.

Of the sulfur-containing products derivable from the various processes evaluated, ammonium sulfate appeared to be the least desirable, at least in this country, for the following reasons:

- Ammonia, ammonium nitrate, and urea, all of which contain a much higher percentage of nitrogen than that in ammonium sulfate, are readily available as fertilizers.
- The sulfate radical contributes very little to the nutrient value of ammonium sulfate when this compound is used as a fertilizer.
- The removal of sulfur, in the form of ammonium sulfate, from the flue gas derived from only three 1400 megawatt power plants would supply the present market for ammonium sulfate in this country.

For the above reasons it was decided to eliminate, as a candidate for further study in Phase III, any process which affords ammonium sulfate as the major salable product.

b. Processes Eliminated

Although high capital investment was not considered as the only criterion for rejection of a specific process, the high investment is reflected in the operating cost by the contribution of depreciation and other fixed charges. High capital investment and operating costs accounted for the elimination of several processes:

- Haenisch-Schroeder - this process is expensive because of the high cost of stripping SO_2 from large quantities of water.
- Ozone-Manganese Ion - a large, expensive scrubber is needed to compensate for the low absorption rate and capacity. The dilute sulfuric acid generated as a by-product has little utility.
- Basic Aluminum Sulfate, Sulfidine, Wet Thiogen - low capacity in each case results in the need for a large, expensive scrubbing system.
- Mitsubishi Red Mud - although the capital cost is low for this process, the operating cost is high because of disposal of the spent mud. In addition, the amount of red mud available would limit the process to the treatment of flue gas from a single 1400 megawatt plant.

The processes using ammonia as the absorbing medium and which generate ammonium sulfate as the only or major by-product were considered eliminated for the reasons considered in the preceding section. They all require high credits for ammonium sulfate to be attractive. The following processes are included in this group:

- Fulham-Simon-Carves
- Showa-Denko
- Cominco
- Ammonia Hydrazine
- Mitsubishi Manganese Oxyhydroxide
- Mitsubishi Ammoniacal Liquor
- Magnesium Hydroxide

A few processes have the disadvantage that the SO_2 is not recovered in a usable form. The Battersea, Howden-I. C. I., and the Mitsubishi Red Mud and Simplified Lime processes are typical examples. They have the additional disadvantage that the by-products generated cause equivalent contamination in solid form. In the Battersea process, the calcium sulfate produced is discharged into the water source, whereas the filter cake from the Howden-I. C. I. process must be dumped on land or in the sea. In isolated cases, however, where the cost of waste disposal can be substantially reduced, and where this waste would not create a serious solids pollution problem one or more of these processes might be of interest, especially for existing power plants.

c. Marginal Processes

With the elimination of the various processes considered above, only six processes remained for consideration. Three of these are of the same type, and are considered in this section. These include the Zinc Oxide, Magnesium Oxide, and Manganese Oxide processes.

All of the processes of interest are regenerative in the sense that absorbed SO_2 is recovered by calcination of a metal salt. A valueless by-product is produced in each case because of oxidation of the SO_2.

Johnstone[594] considered the use of magnesium oxide in his development of the Zinc Oxide process, and concluded that it is much less desirable on the basis that the calcination temperature is considerably higher for the magnesium compound, and that the decomposition leads to products other than SO_2, the principal one being sulfur trioxide. Thus, zinc sulfite, at 500°C, yields zinc oxide and pure SO_2, whereas magnesium sulfite must be heated to 1000°C, and is partly converted at this temperature to valueless magnesium sulfate. The literature surveyed indicated that loss of SO_2 through oxidation in the Magnesium Oxide process is about twice that in the Zinc Oxide process.

The above arguments were considered to justify the choice of the Zinc Oxide process over the Magnesium Oxide process. Additional factors favoring the Zinc Oxide process are its much lower operating cost, slightly lower capital investment, and the fact that calcium, rather than the more expensive magnesium, is discarded as waste.

The Manganese Oxide process suffers from many of the deficiencies considered above for the Magnesium Oxide process. Although available information was not considered adequate to permit an unequivocal evaluation of the process, it is known that calcination requires temperatures in the range 1000 to 1100°C, and sulfur trioxide appears as a decomposition product in the form of a dilute and valueless mist. Moreover, the process involves an oxidation-reduction reaction, rather than neutralization, in the scrubber, and this results in a relatively long residence time. As in the case of the Magnesium Oxide process, a comparison of the Manganese Oxide process with the Zinc Oxide process showed unfavorable capital and operating costs.

The conclusion which was drawn from the above discussion was that the Zinc Oxide process was much to be preferred as compared to any of the available processes in which SO_2 is regenerated through calcination. Accordingly, the Zinc Oxide process was chosen as a candidate for Phase III, and the Magnesium Oxide and Manganese Oxide processes were rejected.

d. Candidate Processes

With the elimination of the Magnesium Oxide and Manganese Oxide processes, four processes remain, and each of these was considered to be a candidate for continuing effort in Phases II and III. The candidate processes, which will be discussed in turn, are the following:

- Zinc Oxide
- Ammonia-Hydrazine Exporption
- Cominco Exorption
- Mitsubishi Lime

(1) Zinc Oxide Process

Although no recent work has been done on the Zinc Oxide process, the analysis indicated a relatively low capital investment and one of the lowest operating costs for the process. It also has the advantage of generating a desirable by-product SO_2.

A disadvantage of the process is the multi-unit operations needed in the regeneration of the absorbent and in the recovery of SO_2, which in turn implies the need for a relatively large area in which to house the process. Although calcium sulfate is produced in small quantity, it can be considered to represent a further deficiency of the process.

Phase II of the program, which encompasses the overall laboratory effort, was devoted in part to the improvement of the Zinc Oxide process. Areas which were considered of immediate interest included lowering of the temperature required for calcination, preferably to the point of elimination of the calciner so that SO_2 can be recovered through the use of steam; and, elimination of, or at least a significant reduction in , the extent of oxidation, so that little or no calcium sulfate appears as waste. To the extent that oxidation could be minimized, a corresponding simplification in process equipment would be attainable.

Because extensive data were available pertaining to the development of the Zinc Oxide process, the effort on Phase III of the program was concerned initially with this process. Process improvement resulting from the laboratory program in Phase II was to be incorporated in the Phase III effort. The brief Phase II program did not provide any process improvements.

(2) Ammonia-Hydrazine Exorption Process

The economic analysis indicated reasonably low capital and operating costs for this process. The main product is SO_2, as in the Zinc Oxide process, but the by-product in the present case is ammonium sulfate, so that no waste product requiring disposal is obtained. To the extent that anhydrous hydrazine could be sold, this product would also be available from the process on a stand-by basis.

If no hydrazine were sold, no hydrazine make-up would be required except that due to liquid leakage in the system. Losses due to volatility were expected to be small, inasmuch as Johnstone has shown[224] that for sulfite-bisulfite scrubbing media in the temperature range 35 to 90°C even methylamine (boiling point -7°C) is far superior to ammonia (-33°C) in this respect. Thus, on this basis, a scrubber medium containing hydrazine (+114°) should not exhibit a detectable pressure.

The economic analysis for the Ammonia-Hydrazine Exorption process did not include a cost for the synthesis of aqueous hydrazine. This material could be purchased as 85% hydrate for startup and, if no anhydrous hydrazine were sold, as makeup for small plant losses. However, plant makeup could also be supplied in the form of 3% liquor, which could be produced at relatively low cost. Since the latter contains 97% water, its transport to the plant site would be uneconomical; an alternative route would involve the incorporation of a hydrazine miniplant into the flue gas scrubbing complex of sufficient size to just provide for the loss incurred. Although the cost of such a plant was not considered in the Phase I effort, it would be of sufficiently small size so that its effect on the capital and operating costs for the overall process would be nearly negligible. Such a plant could also be considered for use in providing material for the plant startup.

If hydrazine is offered for sale, the size of the miniplant would be increased in a commensurate manner, unless an over-capacity had been allowed originally. The effect on costs would then be more significant, but would be offset by the credit obtained for the hydrazine sold, and in the most favorable case, the overall flue-gas scrubbing facility could be operated at a profit.

The use of hydrazine sulfite-bisulfite as a scrubber medium appeared highly desirable when compared with other sulfite-bisulfite systems, from the standpoint of capacity of the scrubber for SO_2. Thus, Johnstone[224] noted that although sodium sulfite-bisulfite had the advantage of non-volatility, the system capacity was severely limited by the solubility of the salts (approximately 8 moles/100 moles of water). The analogous ammonia system showed good capacity (22 moles/100 moles), but was limited by the volatility of ammonia. The latter not only affected scrubber losses, but implied a limit in the extent to which SO_2 could be regenerated with steam from the ammonia scrubber effluent. In the case of hydrazine, volatility should be negligible. At the same time the melting points of hydrazine salts [e.g., dihydrazine sulfite, m.p. 61°C, dihydrazine sulfate, m.p. 87° (compare ammonium sulfate, m.p. 513° with decomposition)] are such that it appeared that hydrazine sulfite-bisulfite mixtures would exhibit melting points below the normally employed scrubbing temperature for flue gases of 50°C. Thus, the scrubber medium could require no water, although an equilibrium involving a small amount of water would be reached because of the water content of the incoming flue gas, and that introduced in connection with make-up hydrazine. The overall affect would be that of dramatically increasing the capacity of the scrubber for SO_2, inasmuch as water, an inert solvent with little absorbing capacity at 50° for SO_2, for the most part need not be cycled. It may also be noted, in this connection, that molecular oxygen is much less soluble in concentrated salt solutions,[620] so that as the composition of the scrubber medium approaches that of a fused salt mixture the extent of oxidation in the scrubber should be correspondingly reduced.

With respect to the desorption of SO_2 on heating the rich scrubber liquor, Johnstone[224] has shown that the steam requirements can be directly related to the ionization constant of the base from which the scrubber liquor is formulated. The ideal base constant has been determined to be approximately 10^{-8}. Weaker bases (such as xylidine, $K_B = 10^{-10}$) are good desorbers but poor absorbers, whereas the reverse is true for stronger bases. On this basis, hydrazine approaches the desired base strength ($K_B = 8.5 \times 10^{-7}$) more closely than any of the other bases which have been considered for flue gas scrubbing (NH_3, $K_B = 1.8 \times 10^{-5}$; CH_3NH_2, $K_b = 4.4 \times 10^{-4}$), and consequently it was believed that the steam requirements for the liberation of SO_2 from hydrazine-based systems would be minimal.

Part of the Phase II effort was devoted to a demonstration of process feasibility. Although hydrazine was found to be an excellent absorber for SO_2, attempts to regenerate the hydrazine for reuse resulted in its being oxidized (see Part Three). Consequently, no work was done on Phase III for the Ammonia-Hydrazine Exorption process.

(3) Cominco Exorption Process

The Cominco Exorption process involves somewhat higher capital and operating costs than those for the other candidate processes. Steam costs and the consequent need for heat exchangers contribute heavily to the overall cost. The process is similar to the Ammonia-Hydrazine Exorption process in that SO_2 and ammonium sulfate are produced as salable products, and no waste is formed. Although the process has been used chiefly in smelter applications, it has also been considered for use with flue gases containing 0.3% SO_2.[213] Of all the ammonia processes considered in Phase I, only the Cominco Exorption process yields SO_2 as the major sulfur-containing product.

Although the two exorption processes considered in this section are of the same type, it was not considered desirable to eliminate either as a candidate process. The Ammonia-Hydrazine Exorption process should exhibit several unique features, as discussed above. However, the process had not been demonstrated, and consequently could not logically be compared to the established Cominco Exorption process. The latter, in turn, would appear attractive if the steam costs could be reduced.

The Phase II effort, as applied to the Cominco Exorption process, was largely concerned with improving the ease of stripping SO_2 from the absorbent. Although it appeared from the experimental results that some reduction in steam costs might be realized, the overall process was still not regarded as economical (see Part Three). As a result no Phase III effort was required for the Cominco Exorption process.

(4) Mitsubishi Lime Process

The Mitsubishi Lime process afford a high quality gypsum, suitable for sale as a constituent of wallboard, and for other less widespread uses. Both capital and operating costs are low, and the latter appears in Figure 37 as being almost independent of the sale of the product. However, if the product could not be sold both a pollution problem and a large disposal cost would result. The process is therefore highly dependent on producing a quality product. This in turn requires the removal of nearly all of the fly ash contained in the flue gas, and this must be accomplished upstream of the SO_2 scrubber.

A disadvantage of the process, although of minor importance, is that of employing a slurry as the scrubber medium. All of the other candidate processes have utilized solutions of salts for this purpose. A more serious disadvantage involves the need for hauling the calcium oxide required for the process to the plant site. In the most unfavorable case this could effectively nullify the credit obtained for the gypsum produced. It was concluded that the process may well be economical only if the power plant to be serviced were near a ready source of lime.

It was planned to pursue the Phase II and Phase III investigation of this process if time was available.

e. Sulfur Dioxide as a By-Product

Since gaseous SO_2 is an immediate product of three of the candidate systems covered in this project, the cost of its conversion to marketable forms of sulfur-containing compounds, viz., liquid SO_2, sulfuric acid, and elemental sulfur, was of considerable interest. Conceivably, it may be advantageous to consider any one of the three conversion routes for different sets of circumstances. An order-of-magnitude cost analysis for each conversion route is given in Appendix B.

D. SELECT PROCESS REFERENCES

This section contains brief statements about references which were considered to be the most pertinent to the various processes evaluated. The reference numbers correspond to the listing in the Bibliography, Part Six.

Fullham-Simon-Carves Process

111. A cost estimate is given.

202. Application of processes using ammonia for reducing the emission of sulfur oxides from sulfuric acid plants is discussed.

237. A rather detailed account. Includes discussion on origin of process, pilot plant at Fulham (2000 cu. ft./min.); 1940 half-boiler scale pilot plant (60,000 cu. ft./min.); laboratory work on the control of the scrubbing process; and the North Wilford pilot plant. Results from different pilot plants given. Process costs included.

358. General description of process given with some emphasis of process chemistry.

446. Process chemistry is described. Applicability based on availability of cheap ammonia liquor and the ammonium sulfate market assessed.

461. Paper gives a detailed account of the process. Gives information on the various pilot plants, viz., the Fulham, and the North Wilford plants. Plant details and material of construction given for the scrubbing system, filter press, autoclave and evaporator. Process costs given.

566. A means for controlling the composition of the scrubbing liquid to a narrow range of ratios of sulfite to bisulfite is described. Such control is necessary to minimize the loss of ammonia vapor.

621. Cost analysis for removing SO_2 from flue gases of a power plant of 20,000-kw capacity considered. SO_2 content of gases treated is 0.083 and 0.30 percent. Estimates based on 90% removal. Process costs compared with those for other scrubbing methods.

639. Brief general description with flow chart. Numerous references cited.

670. General description of process. Flow diagram and numerous graphs giving various physico-chemical data, e.g., SO_2 solubility in water vapor pressures of SO_2 and NH_3 over ammonium salt solutions, etc., are presented. Tables of pilot-plant data given. Numerous references also provided.

673. Thorough coverage of process. Laboratory and pilot-plant studies and operations discussed in detail. Extensive physico-chemical data provided. Many references given.

682. General brief description of process. Flow diagram given.

Showa-Denko Ammoniacal Process

390. Brief general description of process, including flow diagram.

Cominco Process

184. Special features, scope of application, and basic design principles of the treatment methods used at Cominco's metallurgical operations at Trail are discussed. Some cost data are presented.

213. Application of the Cominco process as used at Trail, B.C., for the treatment of gases containing relatively low concentrations of SO_2, e.g., as from coal- and oil-burning power plants, is discussed. Process modifications needed to use the Cominco process for such applications are discussed.

245. The development of the various sulfur-recovery processes at Trail is discussed. Technical and economic considerations are included.

255. Brief general description of process.

271. General brief description of process. Flow diagram given.

397. General discussion of the pollution problems created at Cominco's operations at Trail, B.C., and the control methods introduced to solve such problems.

445. Discussion of the application of the Cominco process for treatment of the exit gas from a sulfuric acid plant at Avonmouth, England. Scrubbing system is designed to handle 32,500 cu. ft./min. Some details of the process are given.

639. Brief general description of process. Flow chart given. References cited.

654. Brief general description of process.

670. General description of process. Flow diagram given. Operating data for various plants, e.g., lead-sintering, zinc-roaster and acid plants presented. References provided.

672. Brief general description of process.

673. TVA studies, related to the Cominco process, which include rather extensive pilot-plant work are discussed.

Cominco Exorption Process

245. General description of process and equipment.

670. Brief description of process.

Zinc Oxide Process

108. Some cost data for the process are given.

142. Process description and costs are presented.

255. Brief general description of process.

307. Brief general description of process.

356. Brief general description of process.

594. This report, compiled by the people who developed the process, is the most informative one available. A complete process description, including an account of all equipment components, is given. Pilot-plant information and data provided. Estimates on plant design, operation, and costs are discussed. Extensive physico-chemical data related to process are given.

621. Cost estimate of Zinc Oxide process given and compared with similar estimates for other processes. A coal-burning power plant of 120,000-kw capacity chosen as a basis. Coal consumption of 1 lb/kwh was used. Flue gas flow of 20,000,000 cu. ft. /hr with sulfur dioxide concentrations of 0.083 and 0.30% were considered. A 90% removal of the SO_2 was assumed.

639. Brief discussion.

670. General brief description of process. Flow diagram given.

672. Brief general description of process.

673. Brief description of process.

Howden-I. C. I. (Cyclic Lime) and Mitsubishi Simplified Lime Processes

15. General description of Mitsubishi Simplified Lime and other processes.

111. The results of cost estimates for this process and the Battersea process are presented. Study based on a coal-burning station consuming 1 million tons per year. SO_2 content of coal is 1-2%. It is assumed that flue gas contains 90% of the sulfur and that SO_2 removal efficiency is 95%.

142. The results of a cost comparative study for the Howden-I. C. I. (Cyclic Lime), Fulham-Simon-Carves, and Zinc Oxide processes are presented. A coal-burning power plant of 120,000-kw capacity, using coal containing 1.5 and 5 weight percent sulfur was considered. The flue gas flow rate was taken as 20,000,000 SCFH with SO_2 concentration of 0.083 and 0.30%.

237. Brief general description of process with emphasis on disadvantages. Latter form basis for development of new process, the Fulham-Simon-Carves process.

255. Brief general process description.

276. The development of the cyclic lime process is discussed. Because of the risk of scrubber blockages by calcium sulfate scale, a study designed to ascertain the mechanism of scale formation was conducted; the results are reported.

307. Brief general process description.

312. Physical and chemical problems associated with the Howden-I.C.I. process are discussed.

328. The process is discussed in considerable detail. Description and design principles of the complete process are presented. Process chemistry, prevention of scaling, and operational control are discussed. The pilot plant at Billingham is described. The application of the process to large boiler plants is also considered. A cost analysis for several cases, e.g., for a power plant of 120,000-kw capacity, is also given.

356. General description of process with flow chart. Some discussion of historical development, particularly as related to Battersea process, is given.

358. A brief review of the process is given. Flow chart and some cost data presented. Other processes, e.g., Battersea and Fulham-Simon-Carves are also considered.

538. The occurrence of calcium sulfate crystallization and a method of circumventing the problem are discussed.

621. Cost estimates of the Howden-I.C.I. process given and compared with similar estimates for other processes. A coal-burning power plant of 120,000-kw capacity chosen as a basis. Coal consumption of 1 lb/kwh was used. Flue gas flow of 20,000,000 cu. ft./hr with sulfur dioxide concentrations of 0.083 and 0.30% were considered. A 90% removal of the SO_2 was assumed.

639. Brief general description with flow chart. Several original references cited.

654. Brief discussion.

672. Brief general description.

Battersea Process

108. Lists investment cost of \$11 to \$15 per installed kw, and operating cost of 0.3 to 0.6 mill per kwh.

151. Brief. Operating costs alone reported between \$1.25 and \$1.40 per ton of fuel, with totals probably double.

189. Brief. Shows scrubbing efficiency. Other systems discussed.

192. Development data. Comprehensive description of power station installation.

210. General discussion. Test data on catalytic oxidation of SO_2 using manganese and iron.

234. Brief description. Other processes discussed.

237. Brief discussion. Mentions disadvantages of requiring large amount of Thames River water and contamination of the river with $CaSO_4$ solution. Primarily Fulham-Simon-Carves paper.

255. Brief general description with flow diagram. Other processes considered.

307. Brief description. Indicates operating cost of 12 to 15% of the cost of delivered coal. Other processes considered.

356. General discussions concerning pilot-plant research, theoretical considerations, the original and modified Battersea processes, includes flow diagram. Also treats other processes.

Magnesium Hydroxide Processes

541. General description.

639. Brief description. Other processes discussed.

Magnesium Oxide Process

98. General discussion, equipment arrangements and design.

103. Equilibrium relations in the system MgO-SO_2-H_2O (acid region).

594. Shows oxidation data of SO_2 and MgO calcination temperatures.

598. Provides pilot plant results of the equilibrium vapor pressure of SO_2 over various magnesium bisulfite solutions, and the application of the venturi gas scrubber.

639. Brief description. Other general discussions.

Manganese Oxide Process

5. SO_2 used to recover manganese.

132. Equilibria in the systems SO_2-CO_2-MnO.

346. Manganese ore slurry used for absorption.

424. Process description, some laboratory and pilot plant data.

439. SO_2 used to recover manganese.

Haenisch-Schroeder Process

183. General process description.

Wet Thiogen Process

465. General process description.

Ozone-Mn Ion and $MnSO_4$ Processes

105. Laboratory data.

107. Reactions of SO_2-O_2 in solution of $MnSO_4$.

209. Original laboratory work on the process.

210. Laboratory and pilot plant data. Negative results.

424. Excellent small pilot plant data.

448. Laboratory and pilot plant data.

639. Brief process description.

Sulfidine Process

145. Describes pilot plant work. Unfavorable results. High oxidation, high xylidine losses, excessive steam consumption.

234. Process description. Operations on 5% SO_2 gas.

366. Plant description, flow diagram.

639. Brief process description. High xylidine losses.

670. Process description, flow diagram, cost data.

Basic Aluminum Sulfate Process

10. Describes development of process, flow diagram, plant description.

41. Determination of the extent of the oxidation of the absorbed sulfur dioxide by oxygen.

42. Laboratory packed column data.

224. Vapor pressure data. States that 1% SO_2 gas is lowest that this process can economically treat.

639. Short description of process, unsuitable for gases containing less than 1% SO_2.

670. Brief description of process.

672. Short description.

Mitsubishi Ammoniacal Liquor Process

15. General discussion and flow diagram. Other Mitsubishi processes discussed.

Mitsubishi Manganese Oxyhydroxide Process

15. General discussion. Other Mitsubishi processes discussed.

Mitsubishi Lime Process

15. Brief description. Other Mitsubishi processes discussed.

Wisconsin Electric Power Process

344. General process description and design. Flow diagram.

Wisconsin Electric Power/Universal Oil Products Process

344. General process description and design, capital investment and operating costs.

Combustion Engineering Process

341. Process discussion, development and large-scale operating data, and cost estimates.

486. Process and apparatus description.

Kanagawa Process

62. Brief statement about pilot plant unit in Japan.

257. Discusses salt water absorption system on board ship.

Wellman-Lord Process

429. General discussion with no information on proprietary special treatment.

569. Belgian patent describing process.

Guggenheim Process

635. Brief description.

Diethylene Triamine Process

634. Partial pressures of H_2O and SO_2 over aqueous solutions of diethylene triamine, triethylene tetramine, etc.

635. Laboratory study of absorption of SO_2 by aqueous solutions of diethylene triamine and triethylene tetramine.

PART THREE

LABORATORY EXPERIMENTATION RELATING TO CANDIDATE PROCESSES - PHASE II

I. INTRODUCTION

At the completion of Phase I four processes had been selected for further consideration in Phases II and III:

- Zinc Oxide Process
- Cominco Exorption Process
- Ammonia-Hydrazine Exorption Process
- Mitsubishi Lime Process

II. LABORATORY EFFORT

The laboratory program related to each of these processes is discussed below.

A. THE ZINC OXIDE PROCESS

1. Johnstone Method

a. Process Description

In the Zinc Oxide process the flue gas is scrubbed with an aqueous solution of sodium sulfite and sodium bisulfite. Zinc oxide is mixed with the effluent liquor, forming insoluble zinc sulfite, and regenerating soluble sodium sulfite which is returned to the scrubber. The zinc sulfite is separated by filtration, dried, and calcined to produce zinc oxide, which is returned to the process, and product sulfur dioxide.

Inasmuch as some oxidation occurs in the scrubber to produce sulfate which cannot be readily calcined, the process includes provisions for its removal. The effluent scrubber liquor is treated with insoluble calcium sulfite, and the mixture is passed through a clarifier. The underflow from the clarifier, which contains the calcium sulfite, is acidified with a portion of the product sulfur dioxide, thereby causing the calcium sulfite to dissolve. Calcium ion is thus made available for precipitation as calcium sulfate, which is removed by filtration and discarded. The filtrate is treated with lime to precipitate calcium sulfite, and it is then returned to the clarifier. A flow diagram for the Zinc Oxide process is shown in Figure 10.

b. Process Reactions

Scrubber:

$$Na_2SO_3 + H_2O + SO_2 \longrightarrow 2NaHSO_3 \qquad (1)$$

$$Na_2SO_3 + 1/2\,O_2 \longrightarrow Na_2SO_4 \qquad (2)$$

Liming Tank:

$$2NaHSO_3 + CaO \longrightarrow Na_2SO_3 + CaSO_3\downarrow + H_2O \qquad (3)$$

Gasifier:

$$CaSO_3 + H_2O + SO_2 \longrightarrow Ca(HSO_3)_2 \qquad (4)$$

$$Ca(HSO_3)_2 + Na_2SO_4 \longrightarrow 2NaHSO_3 + CaSO_4\downarrow \qquad (5)$$

Mixer:

$$2NaHSO_3 + ZnO + 1\,1/2H_2O \longrightarrow Na_2SO_3 + ZnSO_3\cdot 2\,1/2H_2O\downarrow \quad (6)$$

Calciner:

$$ZnSO_3\cdot 2\,1/2H_2O \longrightarrow ZnO + SO_2\uparrow + 2\,1/2H_2O\uparrow \qquad (7)$$

c. Process Simplification and Improvement

(1) Introduction

Attempts to improve the Zinc Oxide process included the following concepts:

- The use of monovalent ions other than sodium ion in the scrubber as a means of increasing scrubber capacity.

- Lowering of the calcination temperature required for the thermal decomposition of zinc sulfite.
- Reduction of the extent of oxidation in the scrubber.

Each of these categories will be discussed in turn.

(2) Scrubber Capacity

The capacity of the scrubber for SO_2 (see reaction 1) is dependent on the total Na concentration, C, expressed by Johnstone as moles/100 moles H_2O. Johnstone and Singh[594] found that for $C < 3.5$ reaction 6 occurred exclusively when the rich scrubber liquor was subsequently treated with zinc oxide. At higher values of C a second reaction, competitive with reaction 6, also assumed importance:

$$6NaHSO_3 + 3ZnO + H_2O \longrightarrow Na_2SO_3 \cdot 3ZnSO_3 \cdot 4H_2O \downarrow + 2Na_2SO_3 \qquad (8)$$

Reaction 8 is undesirable because the sodium sulfite component of the double salt does not release SO_2 under normal calcination conditions ($\leq 500^\circ C$).

The tendency of alkali metal ions to form complex salts decreases with increasing charge density, so that Li^+ for example, appeared as a better candidate than Na^+ for avoiding reaction 8. Accordingly an experimental effort was planned in which Li^+, NH_4^+, $CH_3NH_3^+$ and perhaps other monovalent ions would be substituted for Na^+ as a means of increasing scrubber capacity. However, from data obtained in connection with the Phase III effort it was subsequently shown that an increased scrubber capacity would probably not improve the overall economics of the Zinc Oxide process. This arises from the considerations that a certain minimum amount of liquid is required to adequately wet the scrubber surfaces, and that for the quantity of influent gas which must be treated in the practical case the capacity of the scrubber is ample when C is 3.5. Accordingly no experimental work was carried out in this area.

(3) Calcination

The temperature required to release SO_2 from zinc sulfite (see reaction 7) approaches 500°C during the final stages of the calcination. Any substantial lowering of this temperature would be expected to reduce fuel and equipment costs, and accordingly an approach originally suggested by Johnstone et al.[224] for reducing the cost of stripping SO_2 from aqueous ammonia systems was investigated in connection with the calcination problem.[*] As applied to calcination the method involves the addition of a solid acid, HA, to the calciner feed so that the acid anhydride SO_2 is removed from a neutral salt (ZnA_2) rather than a base (ZnO). The desired reaction might be expected to occur at the melting point of the acid (compare reaction 7):

$$ZnSO_3 \cdot 2\,1/2H_2O + 2HA \longrightarrow ZnA_2 + SO_2\uparrow + 3\,1/2H_2O \qquad (9)$$

If an acid were used in this manner, the counterpart of reaction 6, in which the acid would be regenerated for further use, would also require demonstration:

$$2NaHSO_3 + ZnA_2 + 2\,1/2H_2O \longrightarrow Na_2SO_3 + ZnSO_3 \cdot 2\,1/2H_2O\downarrow + 2HA\downarrow \qquad (10)$$

Ideally the acid should exhibit the following properties:

- Sufficient acid strength to promote reaction 9 at the melting point of the acid
- No extraneous functionality, such as halogen, which might promote side reactions
- A melting point in the approximate range 70° to 150°C. The lower limit implies that the acid should be solid at the scrubber temperature (50°C) to permit coprecipitation with zinc sulfite (reaction 10). The upper limit is considered to be defined by the maximum temperature at which steam might be conveniently utilized for the calcination step (reaction 9).

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[*] The original concept of Johnstone is considered in II, B, relating to the Cominco Exorption Process.

- Non-volatility at the calcination temperature
- A relatively low molecular weight

In addition the acid should be inexpensive, and readily available in quantity.

The only acids which appeared to satisfy the above requirements were α, ω-dicarboxylic acids containing four to eight carbon atoms. The best candidate was considered to be azelaic acid ($C_9H_{16}O_4$). All of the acids of interest exhibit molecular weights of less than 200, which is approximately the same as that of $ZnSO_3 \cdot 2\ 1/2H_2O$ (190). A preliminary economic analysis indicated that if the weight of the calciner feed were increased by a factor of two, and if the regeneration could be effected with steam at, say, 100°C, a substantial cost reduction could be realized. For a dicarboxylic acid reaction 9 becomes

$$ZnSO_3 \cdot 2\ 1/2H_2O + H_2A \longrightarrow ZnA + SO_2 \uparrow + 3\ 1/2H_2O \qquad (11)$$

Preliminary experiments with the candidate acids indicated that SO_2 was partially evolved in accordance with reaction 11 at the melting points of the acids. The presence of liquid water tended to promote the reaction, perhaps through ionization of the acid. Inasmuch as the melting points of all of the acids were above the normal boiling point of water, and since little or no SO_2 was evolved until the acids melted, it was considered that a mixture of candidate acids which melted below 100°C would offer the best medium in which to retain the liquid water required to promote reaction 11.

Of various binary acid mixtures only those involving azelaic and sebacic ($C_{10}H_{18}O_4$) acids melted in the desired temperature range. For these acids the eutectic occurred at approximately 80% azelaic acid, and melted at 90° to 93°C. Subsequent experiments with the eutectic mixture and water showed that SO_2 was initially evolved at 90°, but that gas evolution could not be maintained unless the added water was also volatilized. From this observation, which is undesirable from an economic standpoint, and the further observation that SO_2 is readily liberated from aqueous K_2SO_3 by sulfuric acid at room temperature, it was concluded that an acid exhibiting an ionization constant greater than that of azelaic acid (2.5×10^{-5}) would better promote Reaction 11. However, no such acid was found which would also meet the many requirements noted above.

Several quantitative experiments were carried out with the candidate acids in which excess water, or acid, or both were utilized. The best systems were those containing both excess water and acid, but no more than half of the SO_2 was evolved without boiling the water. The following table summarizes the experiments conducted, where A = azelaic acid, S = sebacic acid, AS = the eutectic composition, Z = $ZnSO_3 \cdot 2\ 1/2H_2O$, W = water, and X indicates a four-fold excess of the constituent designated. When no excess of acid was used the ratio of total acid to Z was always unity. The evolved SO_2 is expressed as a percentage of that available in Z, and was obtained after 20 minutes of heating.

System	Bath Temperature ($^{\circ}C$)	$\%SO_2$
A - Z	115 - 125	27.6
A - Z - XA	115 - 125	25.2
A - Z - XA - XW*	95 - 100	35.8
AS - Z	105 - 110	23.2
AS - Z - XW*	95 - 100	24.3
AS - Z - XAS - XW*	95 - 100	50.7

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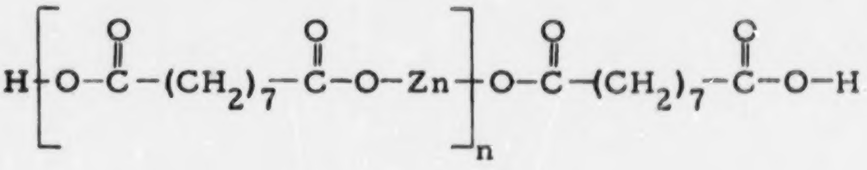
* Based on water in $ZnSO_3 \cdot 2\ 1/2H_2O$

A clear melt was not obtained in any of the experiments shown in the table, and it is believed that the insolubility of ZnA may therefore be a limiting factor in the evolution of SO_2, even if the water is boiled. Although $ZnSO_3 \cdot 2\ 1/2H_2O$ may also be insoluble, this material is subject to a heterogeneous reaction with the liquid acid (reaction 11), and should therefore react completely unless product ZnA forms an insoluble coating on the unreacted sulfite.

Presumably an acid giving rise to a liquid ZnA would be desirable, even if the latter were immiscible with the liquid acid.

Preliminary experiments involving various ZnA derived from the candidate acids indicated that in all cases the zinc compounds were infusible solids, which gradually darkened in color on heating to 300°C. This may be attributable to the dibasic nature of the parent acid, in that ZnA may be polymeric;



$$H\left[O-\overset{\overset{O}{\|}}{C}-(CH_2)_7-\overset{\overset{O}{\|}}{C}-O-Zn\right]_n O-\overset{\overset{O}{\|}}{C}-(CH_2)_7-\overset{\overset{O}{\|}}{C}-O-H$$

In the case of monocarboxylic acids, e.g. lauric acid, polymer formation cannot occur, and the corresponding ZnA_2 are fusible:

$$Zn(C_{12}H_{22}O_2)_2$$

zinc laurate, m.p. 128°C

However, from the standpoint of molecular weight, melting point, and other properties, monocarboxylic acids are not suitable candidates for effecting Reaction 9.

In summary, it is concluded from the above results that the use of a weak acid no longer appears promising as a means of lowering the decomposition temperature of zinc sulfite. If such an acid is used, water will have to be boiled in order to efficiently remove SO_2, and the reaction may still not go to completion because of the insolubility of ZnA in the medium.

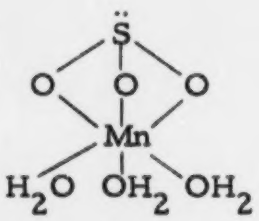
(4) Oxidation

According to Johnstone and Singh[594] at least 10 per cent of the available sulfite is oxidized to sulfate in the Zinc Oxide process. The oxidation occurs mainly in the scrubber:

$$Na_2SO_3 + 1/2O_2 \longrightarrow Na_2SO_4 \qquad (2)$$

The oxygen required for Reaction 2 is present in the flue gas, and the reaction occurs most readily in dilute scrubber media, where the solubility of oxygen is relatively high.

Reaction 2 is catalyzed by transition metal ions, particularly Mn^{++}, Fe^{++}, and Fe^{+++}. The number of d orbitals available in these particular ions is such that the following type of structure can be written, with $SO_3^{=}$ contributing electron pairs:



I

It is postulated that Structure I is important to the oxidation process in that the normally resonance-stabilized sulfite ion is rendered tetrahedral, so that the electron pair shown on sulfur is readily available for oxidation:

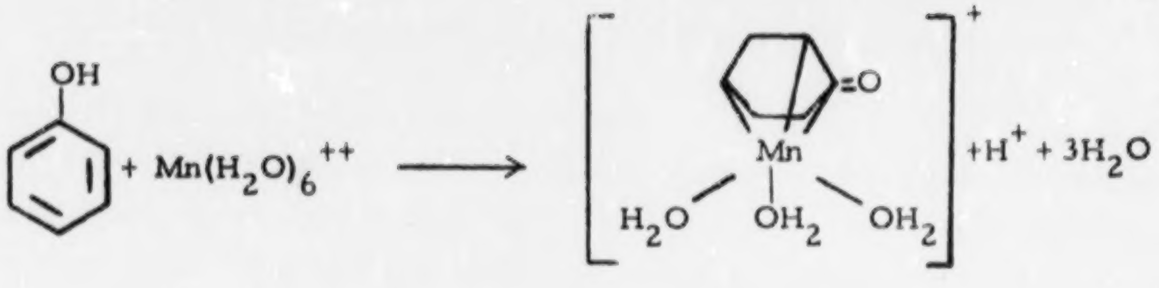
$$I + 1/2O_2 + 3H_2O \longrightarrow Mn(H_2O)_6^{++} + SO_4^{=} \qquad (12)$$

As a result of Reaction 12, manganese ion is made available for further complexing:

$$Mn(H_2O)_6^{++} + SO_3^{=} \longrightarrow I + 3H_2O \qquad (13)$$

Thus, Mn^{++} functions as an oxidation catalyst.

It has been shown[594, 644] that phenols are specific agents for the inhibition of the oxidation of $SO_3^{=}$. It is believed that this is to be attributed to the formation of a stable metal complex involving the phenol, so that the metal ion is then no longer available for oxidation catalysis:



(14)

II

Structure II, which involves octahedral bonding (d^2sp^3) of the manganese, is structurally related to the arene type of complex, of which dibenzene-chromium, $(C_6H_6)_2Cr$, is an example.

From the above discussion, it is concluded that in principle it should be possible to effectively inhibit the oxidation observed in the Zinc Oxide process through the use of phenols, and this in turn would result in a substantial savings in chemicals cost (lime), waste disposal ($CaSO_4$), and equipment sizing. However, it was found in practice that the addition of hydroquinone (a highly effective phenolic inhibitor) to the scrubber used in the Zinc Oxide process had essentially no effect on the extent of oxidation.[594] A probable explanation is that rusted plant surfaces provided enough dissolved iron so that the amount of inhibitor added was insufficient for complexing. In this connection calculations have shown that the iron content of make-up water is insignificant, and that the latter should therefore require a negligible amount of inhibitor.

If the above explanation is correct, it should be possible to inhibit the oxidation of sulfite through the employment of an effective inhibitor used in conjunction with a scrubber which is constructed of non-ferrous metals (or plastic) throughout. This argument presupposes, however, that no fly ash is present. Inasmuch as fly ash normally contains iron oxides as a major constituent, and since the scrubber medium for the

Zinc Oxide process is maintained acidic, the amount of dissolved iron from this source would require the use of a prohibitive amount of inhibitor, unless the fly ash were nearly completely removed upstream of the scrubber.

The Wellman-Lord (Beckwell) process is an example of an aqueous scrubbing process in which fly ash is largely removed from the influent gas before scrubbing. The initial process step involves the use of a water prescrubber, which removes the soluble portion of the fly ash, most of the insoluble particulate matter, and any SO_3 which had preformed as a flue gas constituent. This method may also be applicable to the Zinc Oxide process, and in the most ideal case no inhibitor would be required. It should be pointed out, however, that if an inhibitor were required the process would have to provide for a liquid effluent waste stream, so that soluble complexes involving a cation of the type shown as Structure II could be removed from the system. The present candidate Zinc Oxide process provides only for the removal of a solid waste, in the form of calcium sulfate (see Reaction 5).

The use of a prescrubber for the Zinc Oxide process was considered to be of sufficient interest to warrant an experimental effort. Such an effort would involve a determination of the extent to which oxidation occurs in a non-ferrous scrubber, when an aqueous prescrubber is used to remove the soluble iron portion of the fly ash; and, the use of phenolic inhibitors, if necessary, in the scrubber, as a means of combating oxidation resulting from the presence of any iron which had not been removed by prescrubbing. It was considered that the results of this investigation should be generally applicable to aqueous scrubbing, inasmuch as many of the absorbents for SO_2 which have been used in aqueous media are oxidizable. Although some fabrication of equipment was accomplished for conducting work in this area, time and funding for Phase II were not sufficient to work in the test program. These studies were accomplished, however, in Phase IV (see Volume II).

2. Fluidized Bed Method

a. Process Description

From equations 1 to 7 it appears that the candidate Zinc Oxide process requires the use of Na, Ca, Zn, and H_2O for the absorption and processing of SO_2. In essence Zn acts as the most important of the chemicals employed, since it is from $ZnSO_3 \cdot 2\,1/2H_2O$ that the SO_2 is finally obtained. It was considered of interest, therefore, to determine whether ZnO could be used for the direct absorption of SO_2. If this could be accomplished in a fixed bed, or preferably in a fluidized bed, neither Na nor liquid H_2O would be required, and inasmuch as the only function of Ca is that of coping with the oxidation of sulfite (Reaction 5), it was further considered that this element might also not be required. This would be made possible by resorting to the aqueous leaching of any $ZnSO_4$ formed from the insoluble sulfite. Although water would be used in this step, the few bed volumes needed would be small relative to the total water used in the Johnstone process, where in the scrubber alone C has the relatively low value of 3.5. The $ZnSO_4$ solution, which could be of relatively small volume in view of the high solubility of $ZnSO_4$, would be evaporated to dryness, and the solid returned for credit against the ZnO makeup required.

The envisioned process was therefore one in which the flue gas, after passage through a prescrubber to remove SO_3 and fly ash, would be passed through a fluidized bed of ZnO for absorption of SO_2. The amount of water in the gas phase would be more than sufficient to permit the formation of hydrated zinc sulfite. The latter would be calcined, as in the Johnstone process, for the recovery of SO_2 and the regeneration of ZnO, which would be returned to the bed. Depending on the extent of oxidation, a portion of the bed material would be leached with water to remove sulfate.

b. Process Reactions

Absorber:

$$ZnO + SO_2 + 2\,1/2H_2O \longrightarrow ZnSO_3 \cdot 2\,1/2H_2O \qquad (15)$$

$$ZnSO_3 \cdot 2\,1/2H_2O + 1/2O_2 + 3\,1/2H_2O \longrightarrow ZnSO_4 \cdot 6H_2O \qquad (16)$$

Calciner:

$$ZnSO_3 \cdot 2\,1/2H_2O \longrightarrow ZnO + SO_2\uparrow + 2\,1/2H_2O\uparrow \qquad (7)$$

c. Demonstration of Process Feasibility

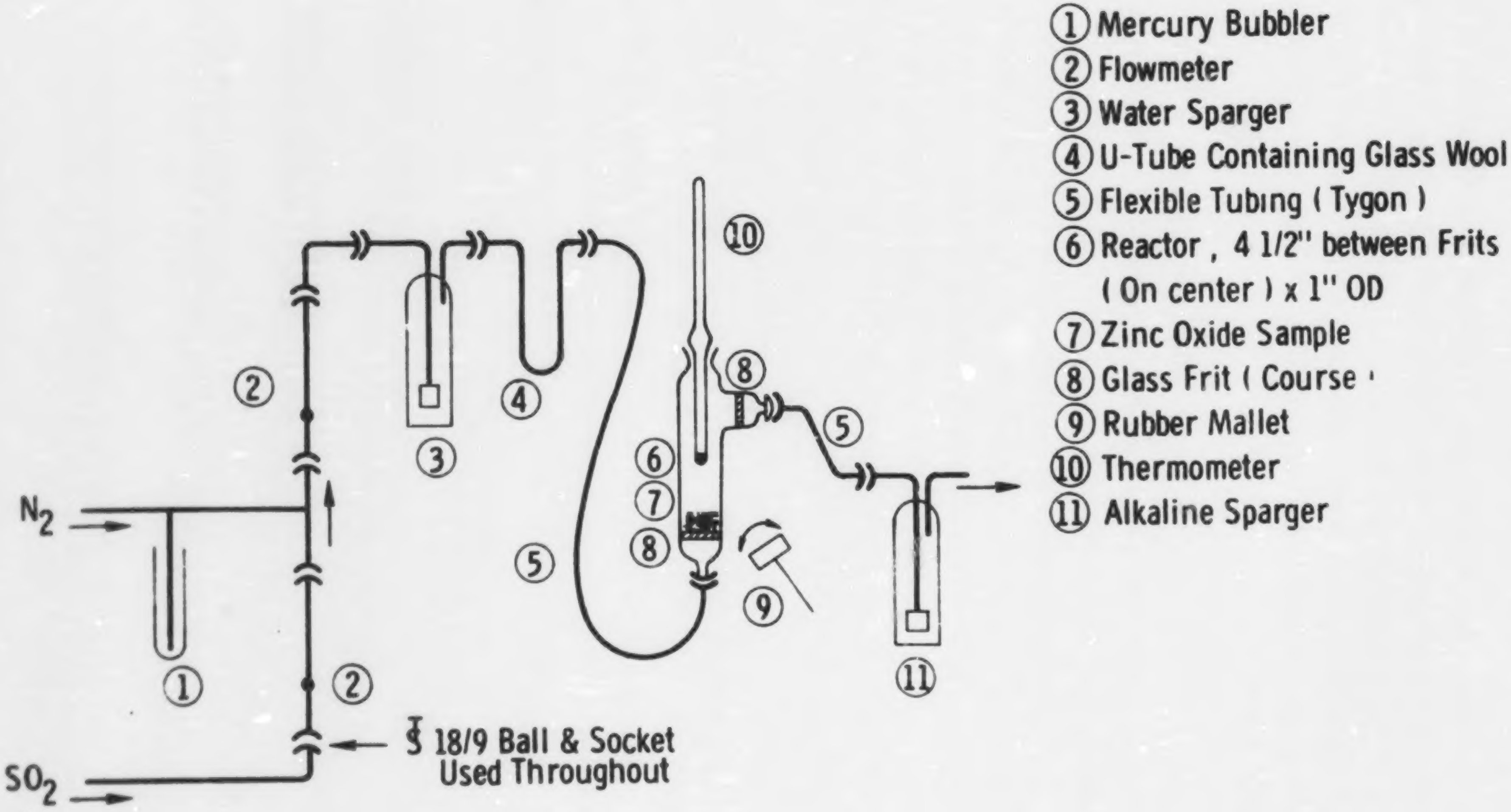
(1) Introduction

Previous data by the Bureau of Mines[29] have shown that solid zinc oxide is ineffective in absorbing SO_2 from flue gas at 130°C and at 330°C. However, it is postulated that the presence of an adsorbed water layer on the zinc oxide surface is required in order to effect the desired neutralization (Reaction 15), and that this condition was not fulfilled at the relatively high temperatures employed in the referenced study. Water is required not only as a highly polar medium in which to effect the reaction, but also for the stabilization of the product through hydration.

(2) Demonstration of Absorption

Initial studies were designed to show that in the presence of sufficient water vapor, and at the prescrubber temperature (50°C), appreciable absorption of SO_2 by fluidized zinc oxide can occur. No attempt was made to approximate the SO_2 content (about 0.3 vol %) of flue gas at this time, but following the demonstration of absorption it was planned to carry out additional experiments in the manner employed by the Bureau of Mines.

The apparatus which was used for the initial experiments is shown in Figure 38. In operation nitrogen gas and SO_2 (The Matheson Co., 99.9%) were separately metered through calibrated flowmeters, and the combined gas sparged through water which had been previously saturated with SO_2. In order to ensure that no liquid water entered the reactor the sparger was followed by a U-trap containing glass wool. As a further precaution in this direction, the sparger liquid was permitted to cool by the sparging of the gas, and was found to reach an equilibrium temperature of about 21°C. Thus the gas entering the reactor was somewhat less than saturated with water at all times. The U-trap was connected to the reactor by means of tygon tubing, in order to provide the flexibility required for the agitation of the reactor. The latter contained two course glass frits, with



① Mercury Bubbler
② Flowmeter
③ Water Sparger
④ U-Tube Containing Glass Wool
⑤ Flexible Tubing (Tygon)
⑥ Reactor , 4 1/2" between Frits (On center) x 1" OD
⑦ Zinc Oxide Sample
⑧ Glass Frit (Course '
⑨ Rubber Mallet
⑩ Thermometer
⑪ Alkaline Sparger
N_2
SO_2
①
②
②
③
④
⑤
⑤
⑥
⑦
⑧
⑧
⑨
⑩
⑪
$ 18/9 Ball & Socket Used Throughout

APPARATUS FOR ABSORPTION OF SULFUR DIOXIDE BY SOLID ZINC OXIDE

Figure 38

the sample placed above the lower frit. Agitation was required to prevent channeling, and was provided by means of a rubber mallet, which in turn was attached to a Burrel wrist-action shaker. The reactor was wrapped with electrical heating tape for runs conducted above ambient temperature. The exit gas from the reactor was passed through aqueous sodium hydroxide to absorb unreacted SO_2.

Three different grades of zinc oxide were examined. Two of these were obtained from the New Jersey Zinc Company, and were designated as Horse Head Kadox—15, 99.7% pure, 0.11 micron mean particle size, and Horse Head XX-504, 99.6%, 1.5 microns. The other material was zinc oxide powder, reagent grade, 99.0%, of unspecified particle size, and was obtained from the Allied Chemical Company. From a comparison of this material with the other two under fluidized bed conditions it appeared that it was probably intermediate in particle size between the New Jersey Zinc Company products.*

The experimental data for a complete run for Kadox—15 at room temperature are shown in Table 68 and a plot of conversion to $ZnSO_3 \cdot 2\,1/2H_2O$ vs time is shown in Figure 39. It will be observed that essentially complete absorption was effected under the conditions employed. Very slight balling of the material was observed to occur during the initial phase of the run, and after 75 minutes the sample was removed from the reactor and

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*Although Kadox —15, of 0.11 micron mean particle size, was used in most of work to be described, it is considered doubtful that such finely divided material is required. Johnstone and Singh[594] observed that their freshly regenerated oxide, which was approximately 30 to 140 mesh, was highly reactive in the sense that complete dissolution of the oxide occurred in aqueous sodium bisulfite solution (see Reaction 6) within "a few seconds." On the other hand, they noted that a commercially obtained oxide required at least two minutes. In the present work it was noted that all of the samples of zinc oxide described above required about three minutes for essentially complete solution in aqueous sodium bisulfite. It would appear, therefore, that commercial zinc oxides may form a monomolecular coating of the less basic zinc carbonate, or perhaps the peroxide, on long exposure to air, and that in consequence freshly regenerated oxide of relatively large particle size may be more reactive than any of the oxides considered here.

TABLE 68

CONVERSION OF SOLID ZnO (KADOX-15) TO $ZnSO_3 \cdot 2\text{-}1/2\, H_2O$ AT ROOM TEMPERATURE - EXPERIMENTAL DATA

Zinc Oxide: 0.856 g

Time (min)	SO_2 Absorbed (g)	Conversion to $ZnSO_3 \cdot 2\text{-}1/2\, H_2O$ (%)	Remarks
-30	-	-	Start
-15	0.000	-	N_2
0	0.010 (H_2O)	-	$N_2 + H_2O$
15	0.183[a]	15.8	$N_2 + SO_2 + H_2O$
25	0.261	22.6	
35	0.339	29.4	
55	0.437	37.9	
75	0.509[b]	44.0	
85	0.570	49.4	
105	0.654	56.6	
130	0.753	65.3	
155	0.825	71.5	
185	0.922	79.9	
215	0.979	84.8	
245	1.025	88.8	
275	1.051	91.2	
305	1.071	92.8	
330	1.077	93.4	
-	1.154	100.0	Theoretical

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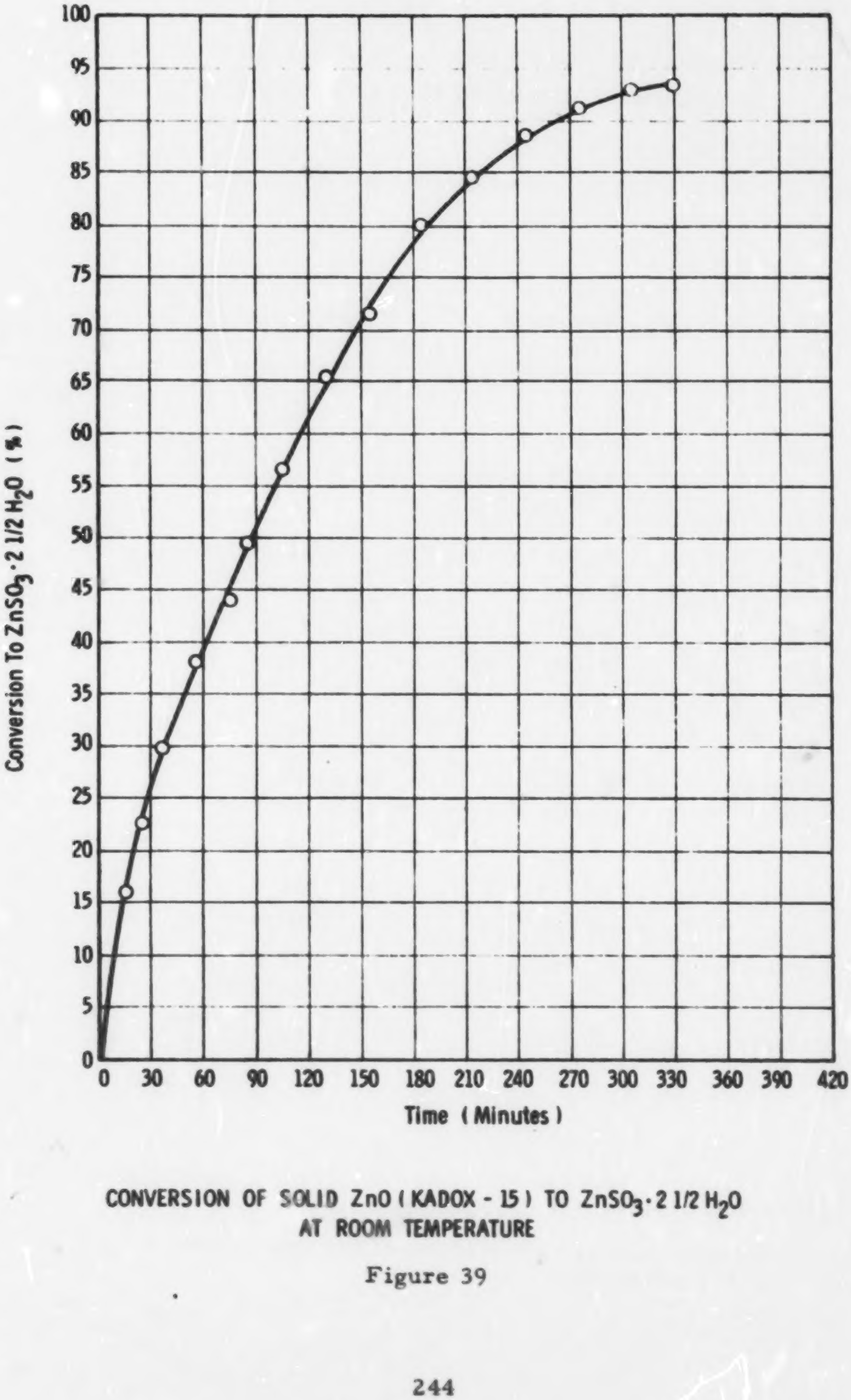
[a] Preabsorbed H_2O (0.010) not included.

[b] Sample removed and ground in mortar; subsequent values corrected for mechanical loss incurred.



CONVERSION OF SOLID ZnO (KADOX - 15) TO $ZnSO_3 \cdot 2\ 1/2\ H_2O$
AT ROOM TEMPERATURE

Figure 39

ground in a mortar. No additional grinding was considered necessary, and the fact that Reaction 16 proceeded essentially to completion, without the necessity for repeated grinding was interpreted as indicating that the zinc sulfite coating is somewhat porous. As indicated in Table 68, the run proper was preceded by a fifteen minute period involving sweeping with nitrogen, followed by an additional fifteen minute period with nitrogen which had passed through a water sparger. This pretreatment was designed to provide a surface layer of water on the zinc oxide before the introduction of SO_2. At the time of introduction of the SO_2 the water sparger was replaced by a sparger containing water which had been saturated with SO_2. The gas flow rates and gas compositions which were used are shown in Table 69. The water content was determined by weighing the sparger initially and after sparging. The final product from the initial run was a free-flowing powder, essentially identical in appearance with the starting material.

Additional experiments were conducted in which the effect of water vapor, particle size, and temperature on the absorption were investigated. It was found that in the absence of water vapor little or no absorption occurred, and that the absorption decreased with increasing temperature at constant humidity. The absorption rate also decreased with increasing particle size of the absorbent, indicating that reaction occurred primarily at the particle surface.

The experimental results described above cannot be directly related to the absorption characteristics of zinc oxide for SO_2 contained in flue gas. Additional experiments were carried out, therefore, in which a fluidized bed of zinc oxide was used under the experimental conditions utilized by the Bureau of Mines in their screening program for metal oxides, but with the following modifications:

- The zinc oxide study was conducted at ≤ 50°C, instead of 130°C and/or 330°C.
- The zinc oxide particle size was smaller than that of the oxides prepared by the Bureau of Mines.

TABLE 69

GASEOUS FLOW RATES AND COMPOSITIONS USED IN REACTOR SHOWN IN FIGURE 38

	Flow (25°C and 752 mm)			Composition	
	l/hr	moles/hr	g/hr	Wt-%	Vol-%
N_2	37.7	1.680	47.1	100	100
N_2	37.7	1.680	47.1	98.4	97.3
+ H_2O	1.00	0.044	0.80	1.6	2.7
N_2	30.5	1.360	38.2	64.2	78.8
+ H_2O	1.01	0.045	0.81	1.3	2.6
+ SO_2	7.20	0.321	20.5	34.4	18.6
N_2	30.5	1.360	38.2	65.1	80.9
+ SO_2	7.20	0.321	20.5	34.9	19.1

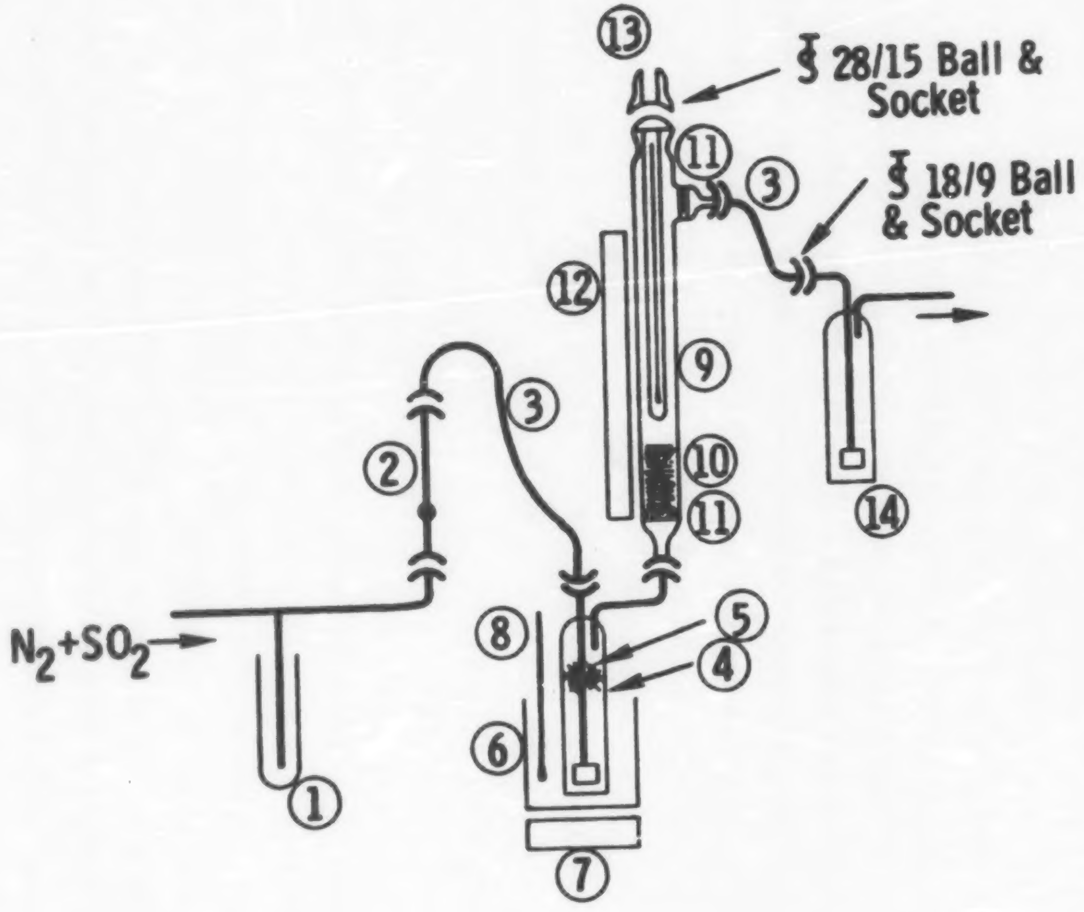
- For simplicity at this time the gas utilized in the present study was 0.27 vol-% SO_2 in N_2; in the Bureau of Mines study CO_2 and O_2 (but no NO_x) was also incorporated in the gas.
- The space velocity [vol of gas (S. T. P.) per hr per vol of absorbent] of 1050 used by the Bureau of Mines corresponded to that employed in the present study for the dry gas (SO_2 in N_2). Following the water sparging operation the space velocity was somewhat higher.

The apparatus which was used is shown in Figure 40. The dry gas was metered at a space velocity of 1050 hr^{-1} into the water sparger, which was maintained at approximately the selected absorption temperature by means of a water bath. Glass wool was placed directly in the sparger unit to prevent the introduction of liquid into the reactor. The upper part of the sparger was wrapped with heating tape, which was extended to include the entire reactor. The latter was similar in design to that shown in Figure 38, but was made longer so that gas entrainment would result in a minimal deposition of solids at the upper frit. The reactor was agitated by means of a vibrating table. A thermometer well was fabricated so that the bulb of the inserted thermometer was in the zone just above the surface of the zinc oxide charge, and was therefore continuously bathed with fluid zinc oxide during the run. Metallic mercury was used for heat transfer in the thermometer well. Unreacted SO_2 in the exiting gas was absorbed in standard 0.1 N I_2, and the excess iodine titrated with standard 0.1 N $Na_2S_2O_3$. The iodine trap was analyzed at selected times during the run.

Preliminary experiments were conducted to determine the efficiency of the iodine trap under operating conditions. In the absence of excess potassium iodide, 25.5% of the contained iodine was lost by volatilization when nitrogen was sparged through the solution for one hour at a space velocity of 1050 hr^{-1}. This loss was decreased to 1.66% through the addition of 5 g of potassium iodide for each 20 ml of 0.1 N I_2 employed, and to 0.54% when a 10 g excess was used. The latter amount was always used during the run, with a correction included for the small iodine loss incurred. Another

Note :

Upper portion of water sparger and entire reactor wrapped with electrical heating tape


13
§ 28/15 Ball & Socket
11
3
§ 18/9 Ball & Socket
12
9
3
2
10
11
14
N_2+SO_2
8
5
4
6
1
7

① Mercury Bubbler
② Flowmeter
③ Flexible Tubing (Tygon)
④ Water Sparger
⑤ Glass Wool
⑥ Water Bath
⑦ Heater
⑧ Thermometer
⑨ Reactor , 15" Between Frits
(On center) x 1" OD
⑩ Zinc Oxide Bed
⑪ Glass Frit
⑫ Vibrating Table
⑬ Thermometer Well and
Thermometer
⑭ Iodine Sparger

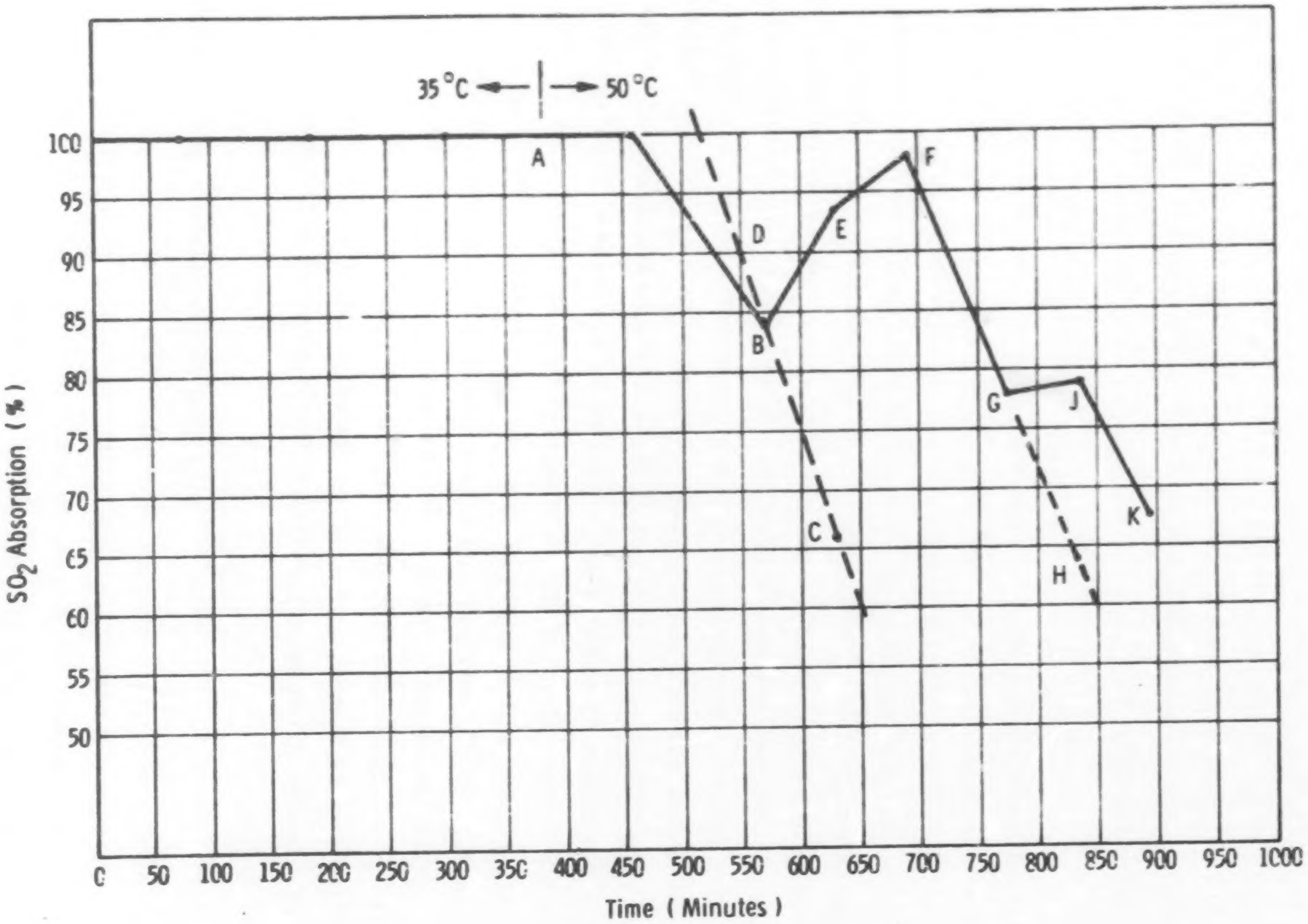
FLUIDIZED BED REACTOR SYSTEM

Figure 40

experiment was designed to show that all of the available SO_2 was absorbed when 0.27 vol-% SO_2 in N_2 was sparged through the iodine solution at a space velocity of 1050 hr^{-1} for one hour. That no SO_2 was lost was shown by back titration with thiosulfate, which indicated a value of 0.27 vol-% SO_2 in the gas, in agreement with the known SO_2 content of the gas as previously determined by mass spectral analysis.

A rather complex run which was carried out with fluidized Kadox -15 is shown in Figure 41, and the corresponding experimental data are given in Table 70. Gaseous flow rates, compositions and wet space velocities used during the run are shown in Table 71. The water content of the gas as indicated in the table is less than that expected for saturation at either 35° or 50°C. This is to be attributed to the fairly rapid rate of sparging, which would both lower the temperature of the water to some extent (compare the above section) and would provide insufficient contact time for saturation. It may be noted that the water content of a typical flue gas without water prescrubbing (which would tend to increase the contained water) is approximately 7.25 vol-%. Inasmuch as saturation of the gas with water was not achieved in the experiment to be described, the experimental data relating to the extent of SO_2 absorption may be considered as conservative in relation to those which would be expected in practice. The run proper, which was initiated at 35°C, was preceded by a water pretreatment period of 105 minutes during which nitrogen gas, which had been sparged through water at 35°C, was passed through the bed. No mechanical difficulties were experienced with the bed during this period or subsequently, and the bed remained highly fluid at all times. Channeling was effectively prevented through the use of the vibrating table.

The first fifteen minute period of the run was allowed for the establishment of equilibrium conditions, including saturation of the water sparger with SO_2. The iodine trap was incorporated into the system at the end of this period, and was removed one hour later for back titration of the excess iodine with sodium thiosulfate. Throughout the run the iodine trap was similarly incorporated into the system for one hour periods, and at the



CONVERSION OF SOLID ZnO (KADOX-15) TO $ZnSO_3 \cdot 2\,1/2H_2O$ IN A FLUIDIZED BED REACTOR

Figure 41

TABLE 70

REACTION OF FLUIDIZED ZnO (KADOX-15) WITH 0.27 VOL-% SO_2 IN N_2 AT 35°C AND AT 50°C; EXPERIMENTAL DATA

Zinc Oxide:	15.8 g
Space velocity of dry gas:	1050 hr^{-1}

Time (min)	Temp (°C)		SO_2 Absorbed (%)	Remarks
	Reactor	Water Bath		
-105	35	35	-	Start
0	36	33	-	$N_2 + H_2O$
15	35	34	-	$N_2 + SO_2 + H_2O$
75	35-1/2	34	100.0	
185	35-1/2	34	100.0	
300	35	33	100.0	Shutdown for inspection of bed.
380	35	33	-	Shutdown overnight; resumed at 50°C.
460	50	48	100.0	
570	50	49	83.9	Shutdown for 3 hours
630	50	48	93.5	Shutdown overnight
690	49	48	98.0	
775	49	48	77.9	Shutdown and maintained system at 50°C for one hour.
835	49	49	78.8	Shutdown and maintained system at room temp. for 50 minutes.
895	49	49	67.3	Total pickup ($SO_2 + H_2O$): 6.6 g.

TABLE 71

GASEOUS FLOW RATES, COMPOSITIONS AND SPACE VELOCITIES USED IN REACTOR SHOWN IN FIGURE 40

	Flow (S. T. P.) (1/hr)	Composition (Vol-%)	Space Velocity (hr^{-1})
N_2	34.1	95.7	1095
+ H_2O[a]	1.43	4.01	
+ SO_2	0.09	0.25	
N_2	34.1	93.9	1118
+ H_2O[b]	2.14	5.90	
+ SO_2	0.09	0.25	

---

[a] H_2O sparger at 35°C

[b] H_2O sparger at 50°C

times indicated by the data in Table 70.

Analyses at 75, 185, and 300 minutes showed that complete absorption of the SO_2 was occurring. The bed was highly fluid during this time, and inasmuch as it was not possible to determine by inspection whether the bed contained liquid water, the run was momentarily interrupted after 300 minutes. It was found, however, that no liquid was present. This was confirmed by noting that the weight gain of the reactor (2.3 g) corresponded almost exactly with that expected (2.2 g) for the conversion of the total SO_2 absorbed during the first 300 minutes to $ZnSO_3 \cdot 2\text{-}1/2H_2O$.

At 380 minutes (shown as A in Figure 41), the run was shut down overnight, and because complete absorption of the SO_2 had occurred up to this point it was decided to resume the run at 50°C. An analysis after 460 minutes showed that complete absorption was still taking place. However, at 570 minutes (B) absorption was incomplete, and from the results obtained by the Bureau of Mines in their screening program, it was considered that the run could be considered as having been nearly completed at this point. In the Bureau of Mines study a given run was continued until the candidate material no longer absorbed at least 90% of the incoming SO_2. In general it was found that absorption was complete until the absorbent was spent, at which time the absorption dropped sharply. In the present study it appeared necessary to obtain only one additional point C, beyond B, so that a line BC could be used to establish the point D, at which a minimum of 90% absorption no longer occurred. From these data one could then calculate the total absorption, in gram per 100 grams of absorbent, for comparison with similar data for the various oxides which were screened by the Bureau of Mines.

Surprisingly the next two points, at E and F, showed appreciable increases in absorption. These increases were well beyond experimental error, and a review of the data indicated that the only unusual circumstance attending points B and E was that in each case the run had been interrupted; at B for 3 hours, and at E overnight. No interruption of the run occurred at F, and the next point, G, showed a considerable decrease in absorption.

Two hypotheses were considered to explain the observed phenomenon. One of these would involve the rupture, on temperature cycling between 50°C and room temperature, of the zinc sulfite coating which had formed on the surface of the zinc oxide during the run, thereby exposing a fresh surface of the oxide to further reaction. It was noted in this connection that the interruption of the run at A had resulted in nearly complete cooling of the solid after only 15 minutes. If this explanation were valid, rapid cooling of the solid at G should show a pronounced effect on the absorption curve, and the otherwise expected point H would not be realized. The other hypothesis is based on the fact that zinc sulfite, unlike the oxide, is slightly soluble in water (0.16 g/100 g at room temperature). This implies that the water present on the solid surface is saturated with zinc sulfite, and that a digestion process might occur in which the zinc sulfite coating continuously dissolves and reprecipitates as a separate crystalline phase. The exposed zinc oxide surface would then become available for further absorption of SO_2. The digestion process would be favored by an increase in temperature. If this explanation were valid, the rapid cooling of the solid would probably not result in subsequent enhanced absorption, since the digestion process would be expected to be quenched in this case. The enhancement of absorption would rather be promoted by interrupting the run, but at the same time maintaining the zinc oxide bed at 50°C until the run was resumed.

The second of the hypotheses considered above was examined first. At point G the run was interrupted, and the system was maintained at 50°C for one hour before the run was resumed. The position of point J, which was subsequently determined, was interpreted as indicating that the digestion process is at least an important factor.

The importance of the rupture of the zinc sulfite coating was examined by quickly cooling the bed at point J through the use of cold air, and subsequently permitting the system to stand for one hour before resuming the run. Heating the system to 50°C was accomplished during the final ten minutes of this one hour period. The next experimental point, K., indicated that temperature cycling was ineffective in promoting the subsequent absorption of SO_2, and therefore that the rupture of the zinc sulfite coating is probably not an important factor.

A few final remarks may be of interest in connection with the experiment described above. The observation that the slope of BE > slope of EF > slope of GJ may perhaps be attributed to the longer time available for digestion at B (3 hours) and at E (16 hours) even though the system was at room temperature during most of the time following B and E. Although the system was also interrupted after 300 minutes, no absorption effect was evident in this case, since complete absorption was still being accomplished at this time. Finally, it may be noted that point D, as indicated in Figure 41, is probably realistic, inasmuch as the slope of the line BC is approximately the same as that of the experimentally determined lines FG and JK.

The theoretical SO_2 pickup per 100 g of absorbent per hour for the system discussed above is 1.66 g. As noted above, this value was precisely realized at the 300 minute point. At point D the SO_2 pickup should have been $515/60 \times 1.66 + (550-515)/60 \times 0.95 \times 1.66 = 15.2$ g. This number may be considered as minimal, inasmuch as the digestion process noted above would normally be expected to enhance the pickup in the practical case, where only part of the spent oxide would be removed for regeneration and the rest would be recycled. To the extent that time would be required for the recycle process, digestion would be expected to occur, so that the recycle feed would possess greater activity than the fresh effluent from the absorber. Table 72 gives a comparison between the results of this study and that conducted by the Bureau of Mines for sodium aluminate and for alkalized alumina. The comparison is necessarily crude, because of the variables involved (temperature, particle size, space velocity, humidity, etc.), but does serve to indicate that zinc oxide should be considered as a candidate for the absorption of SO_2 in a fluidized bed application.

TABLE 72

SULFUR DIOXIDE ABSORPTION BY SELECTED SOLID ABSORBENTS

Absorbent[a]	Purity (wt-%)	Bulk Density (g/cc)	SO_2 Absorbed (g/100 g absorbent)	Temp (°C)
$NaAlO_2$	96	0.90	3	130
Al_2O_3)	73	0.54	18	"
Na_2O)	25			
ZnO	-	-	<1	"
$NaAlO_2$	96	0.90	10	330
Al_2O_3)	73	0.54	17	"
Na_2O)	25			
ZnO	-	-	<1	"
ZnO[b]	99.7	0.48	$\geq$15	50

---

[a] Particle size and space velocity: this study, 0.11 microns and 1118 hr^{-1}, respectively; Bureau of Mines, 8-24 mesh and 1050 hr^{-1}.

[b] This study; all other data taken from the Bureau of Mines study.

The total pickup of water and SO_2, 6.6 g, at the end of the experiment (see Table 70), corresponds to a conversion of 31.0% of the zinc oxide to $ZnSO_3 \cdot 2\text{-}1/2\ H_2O$. The final solid was a free flowing powder, which did not appear to have adsorbed appreciable surface water. A sample of the material was found to lose 9.3% by weight when heated to 105°C for 70 minutes. Commercial $ZnSO_3 \cdot 2\text{-}1/2\ H_2O$ lost 13.8% under the same conditions. In each case some water of hydration was probably lost, in addition to surface water.

Some of the more important conclusions to be derived from this initial Phase II study are the following (see Volume II of this report for additional results associated with the development of this concept and for additional conclusions based on these later results.)

- A fluidized bed of zinc oxide is effective at 50°C for the absorption of SO_2 from a carrier gas containing 0.3 vol-% of SO_2.
- The absorption process is favored by small particle size, low temperature, and the presence of water vapor. If the latter is not present, no absorption occurs; on the other hand, a liquid water phase is not required for absorption.
- Inasmuch as the water content of the gas utilized in the last experiment considered above was less than that required for saturation of the gas, the absorption data obtained from this experiment are considered as conservative in relation to those which would be expected in practice.
- The zinc sulfite coating formed during absorption may be porous to the further penetration of SO_2. An alternative explanation involves a digestion process in which the zinc sulfite coating slowly dissolves in surface water and reprecipitates as a separate crystalline phase. Both concepts may be valid.
- A rough evaluation of the absorption characteristics of zinc oxide indicates that it compares favorably with sodium aluminate and with alkalized alumina for the absorption of SO_2.

- The temperature and humidity of a flue gas following an aqueous prescrubbing step is precisely that required for effecting the absorption of SO_2 by a fluidized bed of zinc oxide; i.e., 50°C and a water content which is near the saturation value.

(3) Calcination

The calcination step for the zinc oxide fluidized bed method is identical with that used in the Johnstone method, as discussed above.

(4) Oxidation

The method envisioned for the separation of zinc sulfite from its oxidation product, zinc sulfate, involves leaching of the sulfate with water, as noted above. Among the relatively inexpensive absorbents for SO_2, zinc appears to be a particularly good candidate for the separation of the sulfite and sulfate in this manner. In the case of alkali metals, for example, both the sulfites and sulfates are soluble in water, and this is also true to a lesser degree of magnesium. On the other hand both calcium sulfite and calcium sulfate are insoluble.

The absorption step for the fluidized bed process is accomplished in the absence of liquid water, and it is of interest to consider whether appreciable oxidation is to be expected under these conditions. In aqueous systems the oxidation process is frequently homogeneous, and typically involves the reaction of dissolved oxygen with the dissolved absorbent (e.g., Na_2SO_3 in the Johnstone process) to give a soluble product (e.g., Na_2SO_4). Of special importance is the fact that the catalysts (e.g., Fe^{+++}) which promote the low temperature (50°C) oxidation process are also water-soluble. In the case of the fluidized bed any catalyst present will necessarily be in the form of a solid, and no leaching of iron from fly ash not retained by the prescrubber will occur. It is also questionable whether appreciable oxygen will dissolve in an adsorbed monolayer of water on the zinc oxide surface. It is believed, therefore, that inasmuch as the conditions leading to homogeneous oxidation catalysis in aqueous scrubbers will not be present under fluidized bed conditions considerably less oxidation will occur in gas-solid systems.

3. Attempted Synthesis of Zinc Pyrosulfite

Some experimental work was carried out on the program in an attempt to prepare zinc pyrosulfite, $ZnS_2O_5 \cdot x H_2O$. A compound of this composition has apparently not been reported. Zinc pyrosulfite would offer the advantage over the simple sulfite of affording two moles of SO_2 on calcination:

$$ZnS_2O_5 \cdot x H_2O \longrightarrow ZnO + 2SO_2\uparrow + x H_2O \quad (17)$$

$$ZnSO_3 \cdot 2\,1/2H_2O \longrightarrow ZnO + SO_2\uparrow + 2\,1/2H_2O \quad (7)$$

The existence of pyrosulfite ions in aqueous solutions of potassium bisulfite is well established, and forms the basis for the Wellman-Lord process for the removal of SO_2 from flue gas. In this process pyrosulfite separates from a cool aqueous solution as a crystalline solid:

$$2KHSO_3 \longrightarrow K_2S_2O_5\downarrow + H_2O \quad (18)$$

Zinc oxide is a relatively weak base, and it is therefore of interest to consider whether the neutralization product zinc sulfite might be expected to combine with an additional mole of SO_2 to form the pyrosulfite. In general this type of reaction occurs only with salts derived from strong bases; for example potassium sulfite combines with additional SO_2 to form the bisulfite in solution, or the pyrosulfite as a water-free solid (Reaction 18). In the case of ammonia, which is comparable in base strength with zinc oxide, the bisulfite forms in aqueous solution, but attempts to isolate either this compound or the pyrosulfite by solvent removal result in a loss of SO_2. This would suggest that either zinc pyrosulfite might be non-isolable or, if isolated, would exhibit a high decomposition pressure of SO_2 at relatively low temperatures. The possibility of preparing the compound was nevertheless considered of sufficient practical interest to warrant a preliminary investigation.

In initial experiments designed to prepare zinc pyrosulfite aqueous solutions of zinc chloride and potassium pyrosulfite (which exists in solution as the bisulfite) were mixed at room temperature, and the resulting solutions cooled to 10°C to induce crystallization:

$$ZnCl_2 + 2KHSO_3 + (x-1)H_2O \longrightarrow ZnS_2O_5 \cdot xH_2O \downarrow + 2KCl \qquad (19)$$

However no precipitate formed, even from solutions nearly saturated with the starting materials at 10°C. It was concluded, therefore, that either the desired compound does not form, or it is highly soluble in aqueous media.

That solid zinc pyrosulfite does not form from solid zinc sulfite and gaseous SO_2 in the presence of water vapor was shown in connection with work reported above relating to the absorption of SO_2 by fluidized zinc oxide. From Figure 39 it appears that solid zinc oxide absorbed approximately 94% of the SO_2 required for the formation of $ZnSO_3 \cdot 2\ 1/2\ H_2O$, with no tendency exhibited toward the absorption of a second mole of SO_2.

Additional experiments were conducted in which an attempt was made to form zinc pyrosulfite in the following manner (compare Reactions 6 and 18):

$$4KHSO_3 + ZnO + (x-2)H_2O \longrightarrow ZnS_2O_5 \cdot xH_2O \downarrow + 2K_2SO_3 \qquad (20)$$

Johnstone and Singh[594] reported that when sodium is used in this type of reaction (see Reaction 6) the zinc oxide completely dissolves before the precipitation of the sulfite occurs. This is important in that the complete solution of the oxide implies that the precipitated sulfite will contain little or no occluded oxide. When the experiment was repeated with potassium, which might be expected to form either the simple sulfite (Reaction 6), the potassium analog of the double salt (Reaction 8), a double salt containing zinc pyrosulfite, or zinc pyrosulfite (Reaction 20), the difficulty was encountered that solution of the zinc oxide could not be effected. Apparently the tendency of potassium toward double salt formation is greatly enhanced over that of sodium, with the result that the formation of an insoluble product occurs almost immediately.

This was observed at C=6, S=5, S/C=0.83, where S is the concentration of available SO_2, in moles/100 moles H_2O, and at C=2, S=1.67, S/C=0.83. Although the observed precipitate may have contained pyrosulfite, it was considered that the occlusion of zinc oxide would render this system valueless in the practical case.

From the results of the above experiments it was concluded that zinc oxide may well be too weakly basic to form an isolable pyrosulfite. Accordingly, work in this area was terminated.

B. THE COMINCO EXORPTION PROCESS

1. Process Description

The Cominco Exorption process involves the scrubbing of flue gas with an aqueous solution of ammonium salts. The off-stream liquor is heated for the liberation of SO_2, the spent liquor then being returned to the scrubber. To the extent that oxidation occurs in the scrubber ammonium sulfate is also produced. The process was used early in World War II when ammonia was in short supply, so that other ammonia-based processes which converted all of the SO_2 to ammonium sulfate (e.g., the Fulham-Simon-Carves and Cominco processes) were less attractive. A flow diagram of the Cominco Exorption process is shown in Figure 8.

2. Process Reactions

Scrubber:

$$(NH_4)_2SO_3 + SO_2 + H_2O \longrightarrow 2NH_4HSO_3 \qquad (21)$$

$$(NH_4)_2SO_3 + 1/2O_2 \longrightarrow (NH_4)_2SO_4 \qquad (22)$$

Heater:

$$2NH_4HSO_3 \longrightarrow (NH_4)_2SO_3 + SO_2\uparrow + H_2O\uparrow \qquad (23)$$

3. Process Simplification and Improvement

a. Introduction

The Cominco Exorption process involves somewhat higher capital and operating costs than those for the other candidate processes (see Figures 36 and 37) and this can be attributed in large part to steam and equipment costs associated with the desorption of SO_2. Accordingly, emphasis in the laboratory was placed on effecting a marked reduction in steam requirements through the use of an acidic type of additive, as considered above for the Zinc Oxide process. However, the physical properties required of an additive for the Cominco Exorption process differ markedly from those required in the case of the Zinc Oxide process. In order to avoid the formation of a slurry in the scrubber, an additive for the Cominco Exorption process should melt below the scrubber temperature of 50°C, and in order to maintain capacity of the ammonia-based scrubber liquor it should preferably be nearly insoluble in the scrubber liquor at this temperature. However, the additive should be highly soluble (but non-volatile) at the stripping temperature, inasmuch as the promotion of SO_2-desorption at approximately 90° to 100°C occurs through solution of the additive. The following equations illustrate the method:

$$NH_4HSO_3 + HA \xrightarrow{90^\circ \text{ to } 100^\circ C} NH_4A + SO_2\uparrow + H_2O \qquad (24)$$

$$NH_4A + SO_2 + H_2O \xrightarrow{50^\circ C} NH_4HSO_3 + HA\downarrow \qquad (25)$$

Another important criterion for a candidate acid additive is that the following relationship should be approached as closely as possible:

$$K_aK_s = 10^{-4.4}$$

where: K_a is the ionization constant of the acid

and K_s is the molal concentration of the un-ionized portion of the acid in solution.

The above equation was derived by Johnstone *et al.*[224] for a partially soluble or partially miscible acid of the type under discussion. When the relationship holds the optimum buffering action in the scrubber commensurate with maximum SO_2 absorption is realized.

b. Desorption of Sulfur Dioxide

The feasibility of using an acid as an additive for the purpose of lowering the steam requirements for the Cominco Exorption process has been demonstrated by Johnstone et al.[222] who measured the partial pressure of SO_2 in ammonium sulfite-bisulfite systems both in the presence and absence of selected acids. A significant increase in the vapor pressure of SO_2 was observed at 90°C with solutions containing, for example, valeric or caproic acid. However, these systems were not considered practical because of various undesirable properties (volatility, high melting point, etc.) of the acids.

As a result of a survey of the various acids which are available in bulk at low cost (OP&D Reporter), it appeared that in all probability no single acid would possess all of the properties considered above. In particular, high boiling acids which exhibit little or no volatility at the temperature of regeneration of SO_2 invariably melt higher than 50°C. It was believed, however, that a mixture of acids might exhibit a eutectic melting well below this temperature, so that over a range of acid compositions the overall scrubber medium would appear as a two-phase liquid system.

Two acids were selected as initial candidates for effecting Reaction 24: azelaic acid, $HOCO(CH_2)_7COOH$, because of its ready availability, low price (36 cents/lb), non-volatility (vapor pressure of 1 mm of Hg at 178°C), and low water-solubility (0.24 g/100 g H_2O at 20°C, and 2.2 g/100 g H_2O at 65°C); and HET (hexachloroendomethylenetetrahydrophthalic) acid, because of its relatively low melting point (70°C), low water-solubility (0.35 g/100 gH_2O at 23°C) and high miscibility with water at 96° to 97°C. It was considered that if either of these acids appeared promising additional effort would be justified involving the use of relatively low melting acid mixtures.

The experimental results obtained with azelaic and HET acids indicated that the major problem area was precisely that previously encountered in connection with the use of acid additives as an aid to the calcination of zinc sulfite (see above); namely, that the desorption of appreciable SO_2 from the rich solution (Reaction 24) required that a relatively large quantity of water be volatilized. Although some reduction in steam requirements appeared to be feasible, the extent of reduction did not appear to justify the use of the acid.

In subsequent work with oxalic acid, $(COOH)_2$, it was found, as had been anticipated, that the high acid strength of this acid permitted the relatively efficient desorption of SO_2. However, the solubility of the acid was such that the Johnstone relation considered above did not hold, and as a result the desorbed solution showed little capacity for the further absorption of SO_2.

C. THE AMMONIA-HYDRAZINE EXORPTION PROCESS

1. Introduction

The Ammonia-Hydrazine Exorption process was conceived at Aerojet, and is similar in principle to the Cominco Exorption process, but potentially free of the most serious difficulty experienced with the latter; namely, the high steam requirements for the desorption of SO_2. Because of the much greater water solubility of hydrazine salts relative to ammonium salts, it was considered that the scrubber liquor for the hydrazine system would contain relatively little water. In fact, the melting points of hydrazine salts in general are sufficiently low* that in the limiting case the scrubber liquor might be comprised of a low-melting eutectic or near-eutectic mixture of salts, with water present only to the extent of an equilibrium amount arising from the flue gas. Under these conditions steam requirements for the desorption step would be minimal, with very little water being volatilized during desorption.

---

* For example, hydrazine sulfate melts at 87°C; compare ammonium sulfate, which melts with decomposition at 513°C.

The process also appeared attractive [illegible] that anhydrous hydrazine, a process intermediate, would represent a saleable product to the extent that a market exists or could be developed, with surplus hydrazine being returned to the process. Makeup hydrazine would be in the form of a dilute aqueous solution, which is commercially available, and which is considerably less expensive than the anhydrous product. Because of the small quantity of makeup likely to be required, the amount of water introduced into the scrubber in this manner would not appreciably affect the overall water content of the scrubber liquor.

2. Process Description

The Ammonia-Hydrazine Exorption process involves the scrubbing of flue gas with a concentrated solution of hydrazine salts. The off-stream liquor is heated for the liberation of SO_2, and the spent liquor is then returned to the scrubber. To the extent that oxidation occurs a portion of the spent liquor is ammonolyzed in liquid ammonia at room temperature to produce ammonium sulfate and anhydrous hydrazine. A flow diagram of the Ammonia-Hydrazine Exorption process is shown in Figure 31.

3. Process Reactions

Scrubber:

$$(N_2H_5)_2SO_3 + SO_2 + H_2O \longrightarrow 2N_2H_5HSO_3 \qquad (26)$$

$$(N_2H_5)_2SO_3 + 1/2O_2 \longrightarrow (N_2H_5)_2SO_4 \qquad (27)$$

Heater:

$$2N_2H_5HSO_3 \longrightarrow (N_2H_5)_2SO_3 + SO_2\uparrow + H_2O \qquad (28)$$

Ammoniator:

$$(N_2H_5)_2SO_4 + 2NH_3 \longrightarrow (NH_4)_2SO_4\downarrow + 2N_2H_4 \qquad (29)$$

4. Experiments Relating to Process Feasibility

a. Absorption Studies

Initial experiments relating to the Ammonia Hydrazine Exorption process were concerned with a demonstration that aqueous hydrazine sulfite represents a suitable absorbing medium for SO_2 (Reaction 26), and with a determination of the extent to which water could be eliminated from the scrubber system. Inasmuch as hydrazine sulfite cannot be obtained commercially, startup was accomplished with aqueous hydrazine;

$$2N_2H_4 + SO_2 + H_2O \longrightarrow (N_2H_5)_2SO_3 \qquad (30)$$

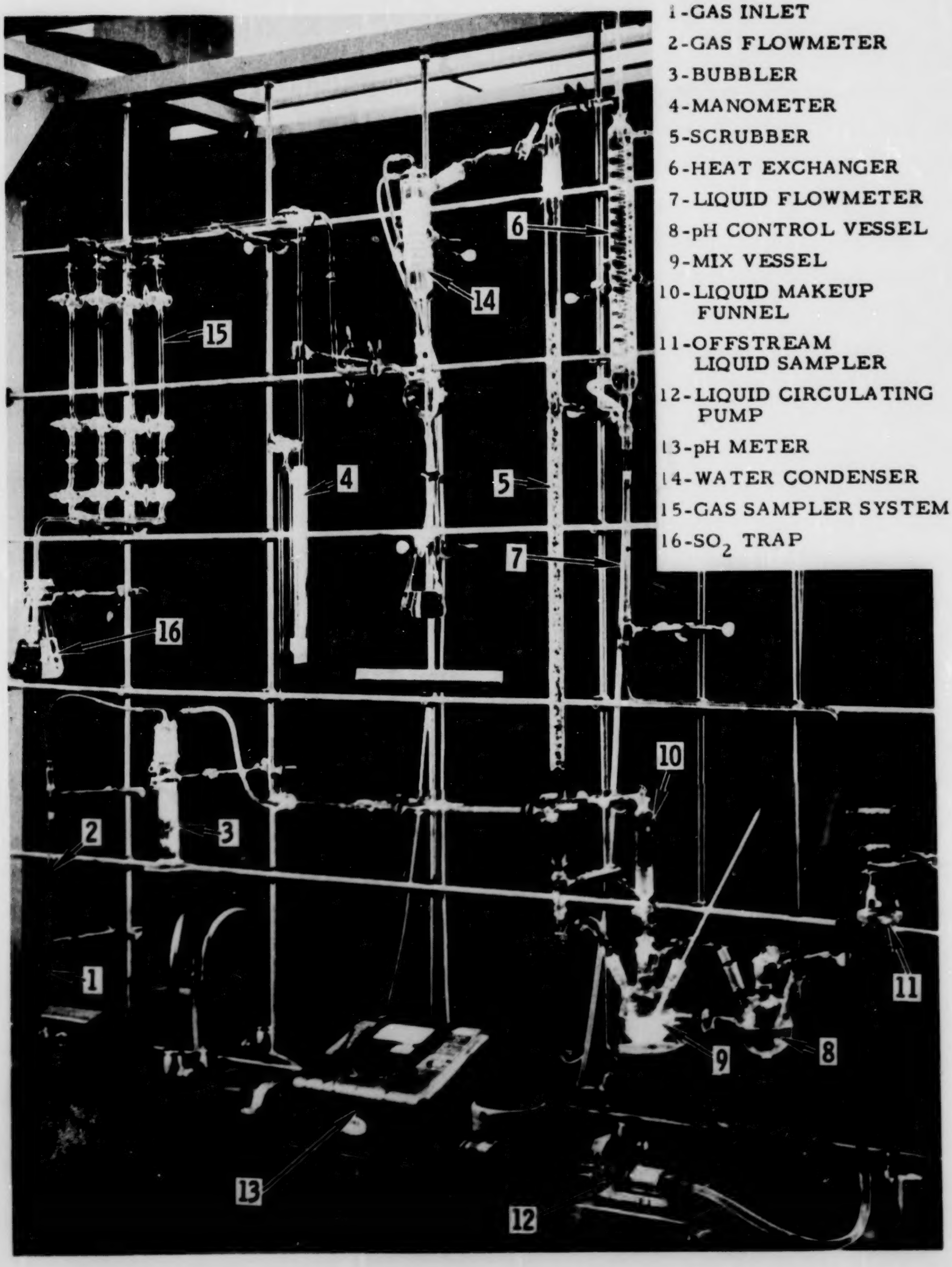
A special apparatus, which was designed and fabricated for investigating the absorption step, is shown in Figure 42. Also, two synthetic gas mixtures were specially formulated (by the Matheson Company) for use in connection with the apparatus. One of these was a mixture of 0.3 vol-% SO_2 and 99.7 vol-% N_2. The other conformed to the composition of a typical flue gas, as shown below, except that water and fly ash were not included in the formulation, and NO_x was considered to be NO_2.

Flue Gas Composition
at 60° F and 1 atm

Component	% by Volume
N_2	74.9
CO_2	14.7
H_2O	7.25
O_2	2.8
SO_2	0.3
NO_x	0.05
Fly Ash	0.2 (by weight)

In initial work the SO_2-N_2 mixture was used for simplicity.

In Figure 42 the gas flows counter-currently to the liquor in the 1-in. dia. scrubber, designated as 5. Cylinder gas enters



1-GAS INLET
2-GAS FLOWMETER
3-BUBBLER
4-MANOMETER
5-SCRUBBER
6-HEAT EXCHANGER
7-LIQUID FLOWMETER
8-pH CONTROL VESSEL
9-MIX VESSEL
10-LIQUID MAKEUP FUNNEL
11-OFFSTREAM LIQUID SAMPLER
12-LIQUID CIRCULATING PUMP
13-pH METER
14-WATER CONDENSER
15-GAS SAMPLER SYSTEM
16-SO_2 TRAP

LABORATORY APPARATUS FOR INVESTIGATING SO_2 REMOVAL FROM FLUE GAS

Figure 42

the system at the gas inlet (1) and passes through a flowmeter (2) and a bubbler (3) (which serves the function of introducing an amount of water into the gas which is roughly equivalent to that shown in the above table) before entering the scrubber. The exit gas, of reduced SO_2 content, is cooled by a water condenser (14) to eliminate excess water, and can then be sampled for gas chromatographic, mass spectrometric, or other analyses in any of four gas sample tubes (15). All exiting gas passes through an alkaline SO_2 trap (16), the contents of which can be later analyzed for SO_2 content.

The counter-current liquid flow from the scrubber passes through a liquid-seal trap to a mix vessel (9), which is magnetically stirred, and into which make-up base (e.g., hydrazine) is added from a dropping funnel (10). The mixture then flows through a pH control vessel (18), which is fitted with appropriate electrodes. The center neck of this flask may contain a hydrometer (not shown), so that continous specific gravity data may be obtained. From the pH control vessel the liquid passes through a plastic-lined circulating pump (12), a heat exchanger (6), which in general maintains the circulating scrubber liquor at about 50°C, and then back to the scrubber. The liquid volume of the system, about 500 ml, is maintained at a constant level through the removal of scrubber liquor to an offstream sampler (11).

Calibration runs were made with 20 molal NH_3 solutions (20 moles NH_3/100 moles H_2O) as the absorbent in order to determine the column absorption efficiency through a comparison with published data. The data given in Table 73 and in Figure 43 show that the extraction efficiency of the 1-in. column is considerably higher than that obtained by TVA workers using 8 ft of 2-in. Raschig rings in a 2-ft. dia. column.[673]

The first series of runs made with a 20 molal hydrazine solution showed that the extent of SO_2 absorption was higher than 93%, approximately the same as for the ammonia solutions of comparable pH. The product gas from Runs H-1 and H-2 (see Table 73), made with the 20 molal hydrazine solution at a 0.45 SO_2/N_2H_4(S/C) ratio, was analyzed for hydrazine and ammonia content as well as for SO_2, but neither of these compounds was

TABLE 73

BENCH SCALE SO_2 ABSORPTION DATA

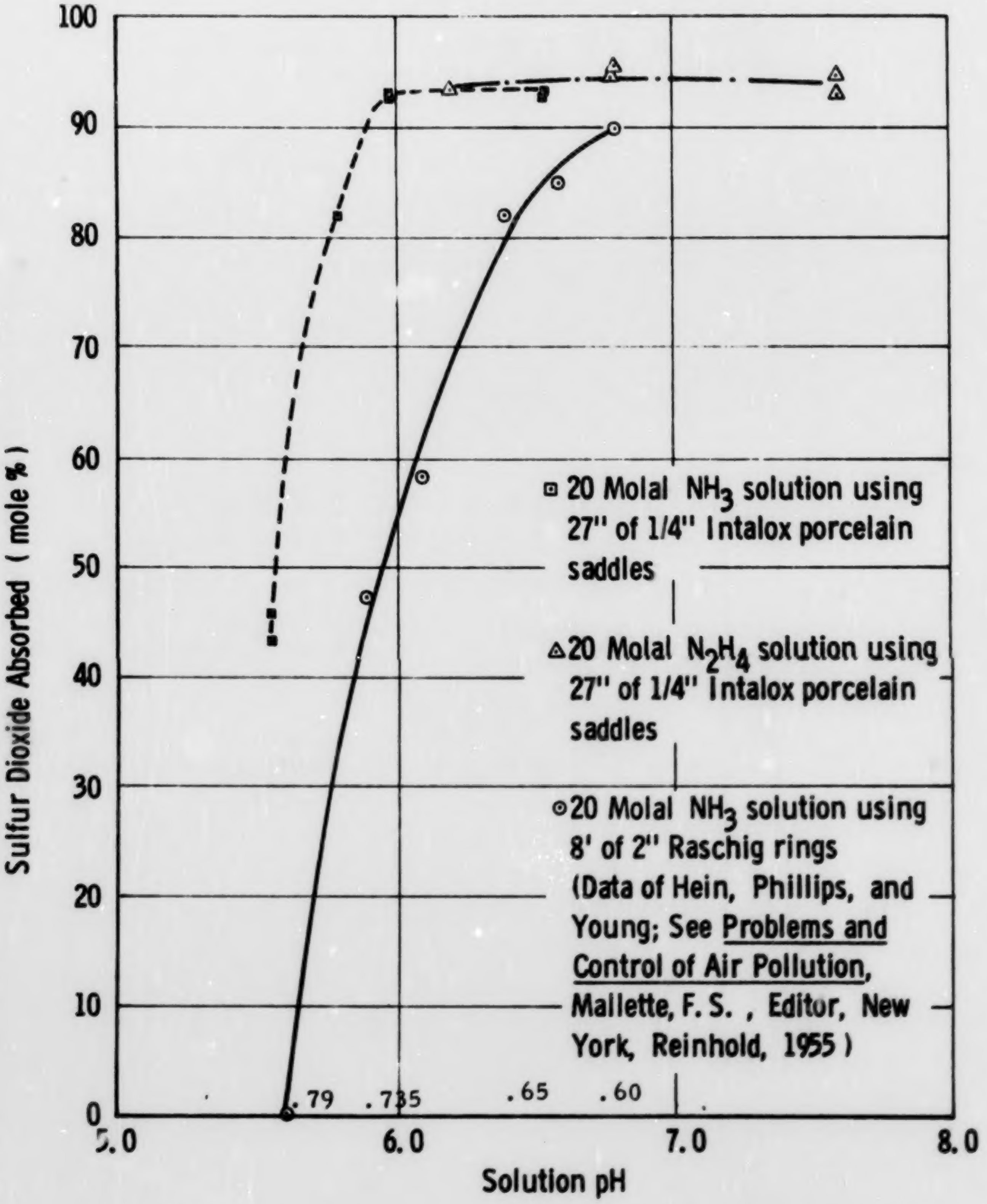
Run No.	Solution Composition $\left(\frac{\text{moles}}{100 \text{ moles } H_2O}\right)$	Flow Rates		Column Δp (mm H_2O)	Solution Temp (°C)	Solution pH	SO_2 in Feed Gas (%)	SO_2 in Product Gas (%)	S/C* Ratio	SO_2 Removal (%)**
		Liquid (ml/min)	Gas (l/min)							
A-1	20 NH_3	178	2.5	18	50	6.55	0.279	0.020	0.60	93.0
A-2	"	"	"	20	50	6.55	"	0.019	0.60	93.0
A-3	"	"	"	18	50	6.00	"	0.021	0.675	92.5
A-4	"	"	"	20	50	6.00	"	0.021	0.675	92.5
A-5	"	"	"	20	50	5.80	"	0.050	0.75	82.0
A-6	"	"	"	19	49	5.55	"	0.155	0.82	44.5
A-7	"	"	"	20	50	5.55	"	0.159	0.82	43.0
H-1	20 N_2H_4	178	2.5	17	50	7.60	0.279	0.018	0.45	93.6
H-2	"	"	"	19	50	7.60	"	0.014	0.45	95.0
H-3	"	"	"	20	50	6.80	"	0.013	0.52	95.5
H-4	"	"	"	22	50	6.80	"	0.018	0.52	95.0
H-5	"	"	"	19	50	6.2	"	0.018	0.60	93.6

---

* S = total concentration of dissolved SO_2 (moles/100 moles water)

C = total concentration of base (moles/100 moles water)

**Determined by passing effluent gas through standard iodine solution which is subsequently titrated with standard thiosulfate (SO_2 is quantitatively oxidized by iodine).



ABSORPTION OF SO$_2$ BY NH$_3$ AND N$_2$H$_4$ SOLUTIONS IN PACKED COLUMNS

Figure 43

detected. The overall test results indicated that a 20 molal hydrazine solution exhibits excellent absorption characteristics for SO_2 when the S/C ratio is in the range 0.45 to 0.60. For an aqueous solution of $(N_2H_5)_2SO_3$ the S/C ratio is 0.50, so that it appears from the data that the sulfite is effective in absorbing SO_2 in the manner indicated in Reaction 26.

When a 50 molal solution was used for absorption it was found that a large quantity of white, needle-like crystals precipitated from the solution when the S/C ratio had increased to a value of 0.45. It was subsequently noted that no precipitate formed from a 45 molal solution under similar experimental conditions. An elemental analysis of the solid indicated that it probably consisted of impure sulfite. The experiment was signficant in indicating the limit to which water could be eliminated from the absorber at 50°C. Although a 50 molal solution (i.e., C = 50) contains much less water than that encountered in other scrubber media (e.g., $C < 20$ for NH_3 systems, and C = 3.5 for the Johnstone Zinc Oxide process) it appeared that the water content of the medium was such that objectionable steam costs would still result. On the other hand the precipitated solid sulfite was readily isolable by filtration, and it was therefore of interest to consider the possibility of thermally decomposing the solid to yield SO_2 (compare Reaction 30):

$$(N_2H_5)_2SO_3 \longrightarrow 2N_2H_4 + SO_2\uparrow + H_2O \qquad (31)$$

Some encouragement in this direction was afforded by the observation that the solid melted with gas evolution at the relatively low temperature of 71°C.

b. Regeneration Studies

(1) Analysis of the Solid

It was noted above that an elemental analysis of the solid obtained from the N_2H_4-SO_2-H_2O system was in reasonable agreement with that expected for the normal sulfite, $(N_2H_5)_2SO_3$. It was considered, however, that the solid might be an isomer of the sulfite, with the structure $N_2H_5^+H_2NNHSO_2^- \cdot H_2O$, inasmuch as the closely related compound

$(N_2H_5^+)_2\ O_2SNHNHSO_2^=$ can be isolated from the system N_2H_4-SO_2-C_2H_5OH.[652] Evidence that the solid was indeed the sulfite was obtained, however, from its reaction with aqueous barium chloride. Barium sulfite of 97.5% purity was precipitated in 89% yield from the reaction mixture. An infrared spectrum of a mulled sample of the original solid also supported the sulfite structure.

An analysis of the solid with aqueous KIO_3[648] indicated a purity of 95.5%, based on the empirical formula $N_4H_{10}SO_3$, and with all of the nitrogen considered to be in the form of the hydrazine moiety. With the impurity presumed to be water, on the basis that the solid was isolated from aqueous solution, the following analytical results are also definitive: Calc'd, for 95.5% $N_4H_{10}SO_3$ + 4.5% H_2O; N, 36.7%; H, 7.04; S, 20.9. Found: N, 37.6; H, 7.47; S, 20.7.

(2) Thermal Decomposition of Solid Hydrazine Sulfite

In an attempt to effect reaction 31 the thermal decomposition of the solid was investigated. No appreciable decomposition was noted below the melting point of the solid at 71°C. At this temperature gas evolution occurred, leaving a colorless, viscous liquid residue which did not solidify at room temperature. It was found, however, that the evolved gas was nitrogen, rather than SO_2 (by gas chromatography). The quantity of evolved gas accounted for the oxidation of approximately one fourth of the available hydrazine in the solid. The remainder of the hydrazine was liberated as such from the solid during the decomposition, and appeared as a less volatile fraction containing appreciable water. Hydrolysis of the non-volatile residue with hot HCl yielded H_2S and elemental sulfur as hydrolysis products, indicating that contained sulfur had undergone reduction during the thermal decomposition.

(3) Thermal Decomposition of Aqueous Solutions of Hydrazine Sulfite

The reducing properties of aqueous hydrazine are much more pronounced in concentrated solution than in dilute solution, and on this basis it was considered that the thermal decomposition of an aqueous solution of hydrazine sulfite might be less subject to oxidation-reduction than that attending the decomposition of the solid. This was found to be the case, but the evolution of nitrogen could not be completely avoided. For example, when a 40 molal hydrazine solution containing 0.97 moles of SO_2 per mole of hydrazine was heated to boiling at 70°C and at a pressure of 20-in. of Hg for 3 hours, about 0.13 moles of N_2 was obtained per mole of hydrazine. Approximately 35% of the SO_2 in solution in excess of that required for an S/C ratio of 0.5 (corresponding to the normal sulfite) was also evolved. In another experiment a 20 molal hydrazine solution with S/C = 0.80 evolved 5.29% of the theoretical nitrogen during two hours at 67° to 73°C.

The above experiments indicate that the thermal decomposition of hydrazine sulfite is attended by the formation of nitrogen under relatively mild conditions. Even a small loss of hydrazine, a relatively expensive makeup chemical, in the form of elemental nitrogen is economically prohibitive, and it was therefore decided to terminate work relating to the hydrazine system.

5. Experiments with Methylhydrazines

A limited amount of experimentation was carried out with monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH) to determine whether these compounds offered any advantage over hydrazine relative to regeneration of the SO_2, as well as of the base. A 20 molal MMH solution was prepared and treated with SO_2 to give an S/C ratio of 0.7. The solution was found to readily absorb SO_2. When heated to the boiling point (108°C), however, the solution liberated 0.21 moles of nitrogen gas per mole of MMH over a 75-min period.

In another experiment a 40 molal solution of UDMH was prepared and treated with SO_2 to give an S/C ratio of unity. When this solution was subsequently heated SO_2, but no nitrogen, was evolved. However the solution had become intensely yellow, and showed little capacity for the reabsorption of SO_2.

D. THE MITSUBISHI LIME PROCESS

1. Process Description

In the Mitsubishi Lime Process sulfur dioxide is scrubbed from the flue gas by a 10% lime or limestone slurry. The actual absorbent is calcium bicarbonate, which is present in solution as the result of an equilibrium reaction with calcium carbonate. A portion of the circulating medium is continually withdrawn and oxidized with air to afford a high purity calcium sulfate (gypsum). The high purity of the product is a consequence of working with a scrubber effluent which is essentially free of fly ash. A flow diagram of the Mitsubishi Lime process is shown in Figure 44.

2. Process Reactions

Scrubber:

$$SO_2 + Ca(HCO_3)_2 \longrightarrow CaSO_3 \downarrow + 2CO_2 + H_2O \qquad (32)$$

$$CaSO_3 + 1/2\,O_2 \longrightarrow CaSO_4 \downarrow \qquad (33)$$

Makeup Tank:

$$CaO + CO_2 \longrightarrow CaCO_3 \downarrow \qquad (34)$$

and/or

$$CaCO_3 \downarrow + H_2O + CO_2 \rightleftharpoons Ca(HCO_3)_2 \qquad (35)$$

Oxidation Tower:

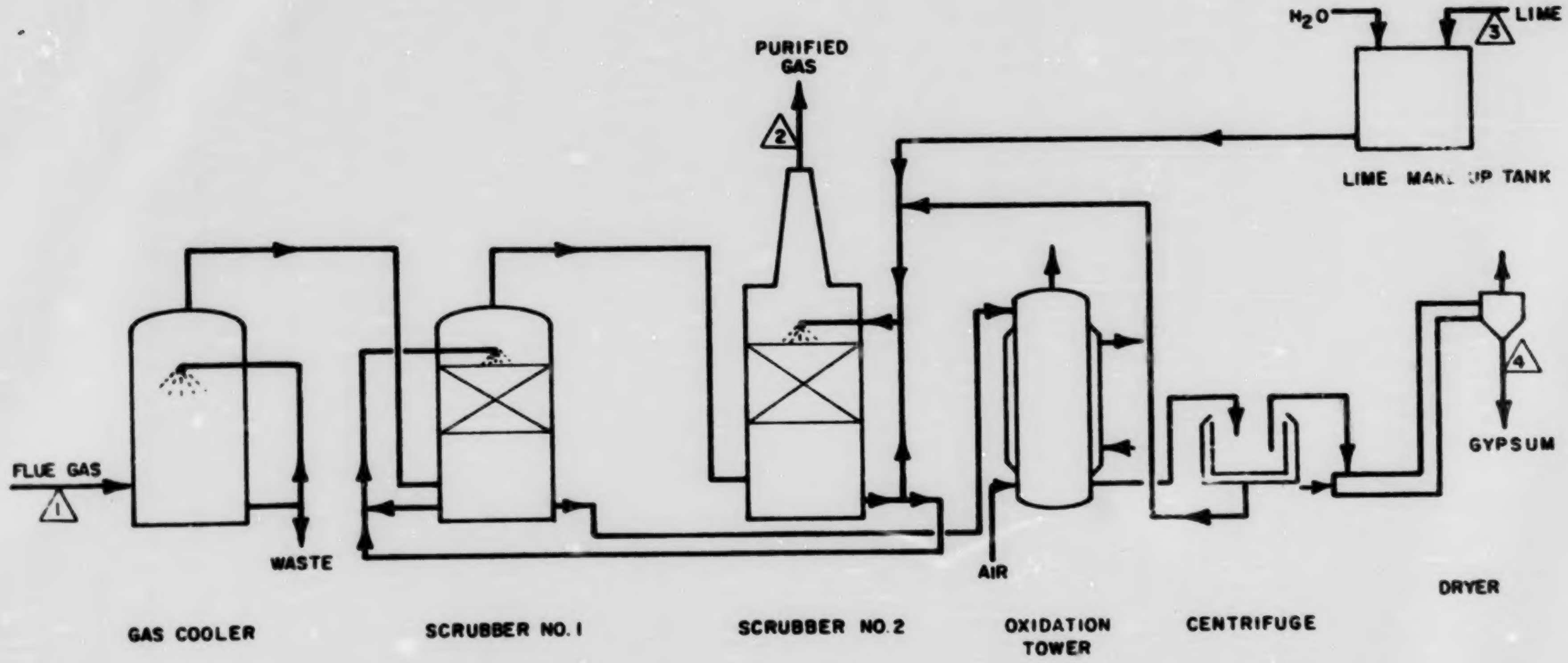
$$CaSO_3 + 1/2\,O_2 \longrightarrow CaSO_4 \downarrow \qquad (33)$$

3. Process Simplification and Improvement

No experimental work appeared to be indicated at this time relating to the Mitsubishi Lime process. The process was regarded as economical, provided that product gypsum could be sold in quantity. This point is considered further in Part Four, IV.A.

Reactant Chemicals Per Million SCF Flue Gas Processed

Stream	Component	Lb Moles	Lbs
1	SO_2	8.36	535
2	SO_2	0.42	26.8
3	Lime (CaO)	7.94	445
4	$CaSO_4 \cdot 2H_2O$	7.94	1367


H_2O
LIME
3
PURIFIED GAS
2
LIME MAKE UP TANK
FLUE GAS
1
WASTE
AIR
4
GYPSUM
DRYER
GAS COOLER
SCRUBBER NO. 1
SCRUBBER NO. 2
OXIDATION TOWER
CENTRIFUGE

MITSUBISHI LIME PROCESS : FLOW DIAGRAM

Figure 44

PART FOUR

PRELIMINARY PLANT-SCALE PROCESS EVALUATION AND COST ESTIMATE - PHASE III

I. INTRODUCTION

The objective of Phase III was to perform preliminary process designs and an economic analysis for each candidate process, as applied to the cases listed below. Data generated in Phases I and II were used as input.

Case	Description	Flue Gas MMSCFM	Exit SO_2 ppm	Coal Requirement tons/hr	Plant Factor days/year	Plant Factor % cap.
1	Large new power plant facility 1400 megawatt	2.5	150	580	330	100
2	Large existing power plant facility 1400 megawatt	2.5	150	580	330	100
3	Small existing power plant facility 220 megawatt	0.5	300	90	330	60
4	New smelter facility (5% SO_2 to scrubber)	0.02	5,000	-	Not Specified	

For Case 4, the extent to which the process would be amenable to fitting into an existing smelter facility was also of interest.

The flue gas composition for Cases 1-3 was considered to be the same as that given in Part Two, III. C. 1. a. of this report. The fly ash content (0.2 wt-%) was presumed to be that which occurs upstream of removal equipment. In existing plants with installed fly ash collecting equipment it was assumed that the fly ash content had been reduced to at least 0.02 weight percent.

An analysis midway in the program indicated that Case 4 as specified above did not apply to a representative smelter operation; therefore, the initial conditions were abandoned in favor of a more typical case.

The new conditions were based on data provided to NAPCA in a progress report by another contractor (Allied Chemical Corp.). The smelter gas in this case is obtained from a medium size copper smelting facility, and consists of the combined process gas from three converters and two medium size reverberatory furnaces fired with coal. The following conditions prevail:

- Converter cycles are scheduled to even out gas composition, which varies from 0-21% SO_2 during one complete cycle of a converter.
- As per standard American practice, air dilution is used to cool the converter gas to protect the collecting system.
- Gases from the reverberatory furnaces (100,000 SCFM) and from the converters (110,000 SCFM) are combined.
- Based on recent data from an actual operating U.S. copper smelting facility, converter gas composition is taken as

  SO_2 - 4.5%
  $O_2 - N_2$ 95.5%

  and reverberatory gas as

  SO_2 - 1.1%
  CO_2 - 3.5%
  CO - 1.2%
  H_2O - 0.23%
  O_2 - 13.0%
  N_2 - 81.0%
  H_2SO_4 - 1.25 lb/min
  Dust - 0.2 grain/SCF

Combining the gases results in the following standard case:

Smelter Gas - 210,000 SCFM (760 mm & 32°F) or 220,000 SCFM (1 atm & 60°F - Phase III conditions).

Gas temperature - 440°F

Component	% by Volume
SO_2	2.9
CO_2	1.7
CO	0.6
H_2O	0.1
O_2	14.3
N_2	80.4
H_2SO_4	1.25 lb/min
Dust	0.2 grain/min

It was assumed that the facility would operate at a plant load factor of 90% or 330 days at 100% capacity.

II. PROCESS DESIGN

A. GENERAL

The process design for each case included the operations listed below:

- The quantity and quality or composition of input gas, exit gas, by-products and "other" raw materials were defined.
- A safety factor of 10% was used for the equipment.
- A preliminary process flow diagram indicating all the operations required was constructed.
- Each unit operation was checked for alternate routes for possible economic advantage.
- Alternate equipment routes for SO_2 absorption were considered. These included countercurrent-flow and cross-flow packed scrubbers, and flooded bed scrubbers (Turbulent Contact Absorber), the latter for slurry systems.
- Material and energy requirements were prepared.
- The utilities needed were specified.

- Absorption towers and strippers were designed with the assistance of equipment manufacturers as needed.

- Design data for other equipment, such as pumps, compressors, heat exchangers, filters, centrifugals, crystallizers, evaporators, agitators, screens, crushers, grinders, settlers, thickeners, etc., were obtained from specifications. The assistance of vendors was requested when necessary.

- A satisfactory material of construction was selected for each item of equipment.

- Specifications for each item of major process equipment were prepared.

- A final process flow diagram showing all major items of equipment, temperatures, pressures, and flow rates in all parts of the process was prepared. Pertinent process design data were indicated. Valves, utility lines, and spare items of equipment were omitted.

B. STACK GAS REHEAT

Reheat of the exit gas is needed to effect buoyancy of the gas and also to prevent a visible plume or condensation of droplets of water from the stack plume. From the standpoint of conservation of energy and money, minimum reheat should be used because tremendous quantities of gases at ambient pressure must be heated. This involves rather large quantities of energy (gas or low sulfur oil) if direct heating is used or very large and expensive heat exchange equipment if indirect heating is used.

Four methods of reheating the exit gas from the aqueous SO_2 scrubbing plants are discussed below:

By-passing a part of the hot untreated gas.— This would be feasible only where less than 90% SO_2 removal is required. If 100% removal of SO_2 is achieved in the treated portion, by-passing 10% of the 300°F untreated gas would give an overall SO_2 removal of only 90% and would result in a temperature rise of only about 18°F in the exit gas.

Heat exchanging the 300°F inlet gas with 122°F exit gas.— This could be done in several ways but all are relatively expensive and would be limited to a reheat of not more than 100°F. One approach is to use a rotating or moving solid heat sink which would contact first the hot gas and then the cold gas, transferring the heat to the latter; this is typified by the operation of a boiler air preheater. In general, this method is used where a temperature differential, ΔT, of 100°F or larger, exists.

A second approach would be to pass the two gases countercurrent through a heat exchanger having an extended surface on both sides of the tubes or interfaces. Using this approach for the larger plant (2.5 MMSCFM feed gas) results in a very high heat exchange surface requirement of 758,000 sq ft. (This is based on a 110°F reheat, a 44°F mean ΔT, based on a correction factor applied to a cross flow shell and 1 tube pass heat exchanger, and a 10 Btu/hr/sq ft/°F overall transfer coefficient.) An overall transfer coefficient of 10 for a gas-to-gas exchanger at atmospheric pressure is not conservative unless a high pressure drop is taken by both fluids. In this case a high pressure drop would require very expensive gas blowers. At an estimated purchase cost of $3.00/sq ft of exchanger surface, the exchanger would cost 2.3 MM dollars or 9.1 MM dollars installed (3.96 factor).

Using a steam coil with extended heat-transfer surface on the gas side of the exchanger.-- This has the advantage of using high-pressure steam which would be available at minimum cost at the power plant. The high steam temperature would give a large ΔT, thus requiring less surface. For example, 800 psig steam would give a 520°F temperature or a ΔT of $520-172^{*} = 348$°F (for a 100° reheat); thus, the surface required would be only 44/348 or about 1/8 that required if the inlet gas were exchanged with the exit gas. The disadvantages of this system would be the still appreciably high cost of the finned tube unit and the additional power required by the flue gas blower due to the additional inch or two of flue gas pressure drop across the finned tube unit.

Direct heating by burners installed in the bottom of the stack. -- This is the method advocated in this report. Either natural gas or low sulfur oil could be used. The lower section of the stack would have to be lined with firebrick in order to withstand the higher temperature; however, this cost would be minor in comparison with the cost of the heat transfer surface required by indirect heating. The flue gas volume would be increased only about 6% for a 100°F reheat (assuming natural gas burned with 10% excess air).

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[*] Average gas temperature

In the initial analyses of Phase III, the gas temperature was increased 50°F from 122° to 172°F. This was changed toward the end of the effort to an exit gas temperature of 200°F.

C. SO_2 RECOVERY

Recovery of SO_2 in marketable forms of liquid SO_2, elemental sulfur and concentrated sulfuric acid was considered. Conversion to sulfuric acid was the only process used in this study, since reliable data were not available for the processes involving liquid SO_2 or sulfur. Conversion of SO_2 to SO_3 was assumed at 96%.

III. ECONOMIC ANALYSIS

A. INTRODUCTION

The economic analysis provided for each case included a capital cost estimate and an operating cost estimate. The format for capital and operating cost estimates were changed slightly from that used in Phase I in order to more nearly conform, when justified, to cost estimates of SO_2 removal systems appearing in the recent literature.

B. CAPITAL COST ESTIMATE

Preliminary capital cost estimates were prepared, with total purchased equipment cost as the basis for a factored cost estimate. Equipment specifications were sent to vendors, who were requested to submit bids.* These costs were used whenever possible. In a few cases it was necessary to supplement these prices with engineering cost estimates. The capital cost estimate summary form is shown in Table 74. The total purchased equipment cost, Item 1, was factored as shown to obtain the other items of fixed capital cost. Table 74 also shows Working Capital as a part of the total investment. Working Capital, derived from fixed capital cost and from the operating cost estimate (see below), included the following items:

---

* The companies who assisted in this phase of the cost estimate are acknowledged in Appendix C-1.

TABLE 74

CAPITAL COST ESTIMATE SUMMARY

	ITEM	(f)	COST - $
1.	Purchased Equipment	1.0	
2.	Erection Labor	0.25	
3.	Foundations and Platforms	0.18	
4.	Piping	0.50	
5.	Instruments	0.10	
6.	Insulation	0.08	
7.	Electrical	0.10	
8.	Process Buildings, Structures	0.25	
9.	Plant Facilities, 5% of 1-8		
10.	Plant Utilities, 7% of 1-9		
11.	PHYSICAL PLANT COST		
12.	Engineering & Construction, 20% of 11		
13.	DIRECT PLANT COST		
14.	Contingency, 15% of 13		
15.	Contractor's Fee, 5% of 13 + 14		
16.	FIXED CAPITAL COST	4.0	
17.	Interest During Construction, 2.5% of 16		
18.	SUB-TOTAL FOR DEPRECIATION		
19.	Working Capital		
20.	TOTAL INVESTMENT		

21. CAPITAL REQUIREMENTS: $_________/kw capacity

- Raw Material inventory - 2 months
- Direct labor - 3 months
- Maintenance - 3 months
- Supplies - 3 months
- Payroll burden - 3 months
- Plant overhead - 4 months
- Fixed cost - 0.5% of fixed capital cost
- Spare parts & miscellaneous - 1.0% of fixed capital cost

Capital required for plume reheat equipment and for the sulfuric acid plants were not included as part of the basic plant cost. These were added as incremental costs since their utility could be applied to other sulfur dioxide recovery processes.

The fourth method of plume reheat described earlier, i.e., direct heating, was used. The capital cost for direct heating is believed to be lower than for any other system considered.

The capital costs for sulfuric acid plants were obtained by using data in two literature sources which discussed costs for sulfuric acid plants of approximately the size required for Cases 1 and 2.[76,260] The requirements for Cases 3 and 4 were factored from the costs of the larger plant.

C. OPERATING COST ESTIMATE

The operating cost estimates were similar to those developed in Phase I. Some changes were incorporated, when considered justified, in order to conform with recent cost estimates of competitive SO_2 removal processes appearing in the literature. Table 75 shows a typical operating cost estimate summary sheet. Cost elements requiring clarification are discussed below.

- Raw Materials and Chemicals

  In Phase I, most of the raw material chemical costs were obtained from the Oil, Paint and Drug Reporter. In the Phase III work, chemical manufacturers were contacted for current prices at the various annual tonnages required.

TABLE 75

OPERATING COST ESTIMATE SUMMARY

	ITEM	TOTAL $	%
1.	Raw Materials & Chemicals		
2.	Direct Labor		
3.	Supervision, 15% of 2		
4.	Maintenance, 3% of fixed capital cost		
5.	Supplies, 20% of 4		
6.	Utilities		
7.	Other		
8.	TOTAL DIRECT COST		
9.	Payroll Burden, 18.5% of 2 & 3		
10.	Plant Overhead, 50% of 2, 3, 4 & 5		
11.	Waste Disposal		
12.	Other		
13.	TOTAL INDIRECT COST		
14.	Depreciation, 11% depreciable capital cost		
15.	Taxes & Insurance, 3% depreciable cap. cost		
16.	Other		
17.	TOTAL FIXED COST		
18.	TOTAL OPERATING COST		100.0

19. Cost: $_______/ton coal, _______mill/kwh

- **Direct Labor**

  The hourly wage rate was $2.75 per hour.

- **Utilities**

  Utilities were charged at the same unit costs as those used in Phase I, as follows:

Steam, M lb	$0.50
Heat credits & debits, MM Btu	0.50
Power, kwh	0.006
Raw water, M gal	0.10
Recirculated water, M gal	0.05
Fuel oil, gallon	0.10

- **Waste Disposal**

  Costs of disposal of waste materials were applied when applicable.

- **Total Operating Cost**

  The total operating cost did not include any credit for by-product sales.

D. PROFITABILITY

The profitability was checked for each system in which the process involved a salable by-product. This was presented in both tabular form and as a break-even chart indicating by-product sales at various price levels.

IV. PROCESSES EVALUATED

A. INTRODUCTION

As mentioned in Part One, four processes of the twenty-two checked in Phase I were selected as candidates for additional effort in Phases II and III. Two of these, the Ammonia-Hydrazine Exorption and Cominco Exorption Processes were eliminated from further contention in Phase III due to the negative results of the laboratory experimentation, Phase II. This left two processes for Phase III evaluation: the Zinc Oxide Process and the Mitsubishi Lime Process.

The Phase III evaluation of Cases 1, 2, 3, and 4 of the Zinc Oxide

Process are reported in detail in this section.

A re-evaluation of the potential gypsum market in the United States led to the conclusion that it may be more realistic to consider a simplified lime process in the Phase III effort rather than the Mitsubishi Lime process. In the former case, gypsum would be disposed of as a waste material along with the fly ash rather than recovered in pure form for marketability as is done in the Mitsubishi Lime process. Accordingly, the Howden-I. C. I. or the essentially equivalent Mitsubishi Simplified Lime process would form the basis for the Phase III study.

Information acquired in a recent conversation with the president of the Southern California Gypsum Association illustrates the dim forecast for promoting the marketability of pure gypsum as obtained in the Mitsubishi Lime process. Natural deposits of gypsum are very widespread in this country and manufacturers using gypsum for wallboard, etc., have acquired large reserves which will last for 20-50 years. Moreover, these manufacturers have substantial investments in mining and transportation equipment needed to exploit these reserves. Accordingly, it is difficult to estimate the cost of gypsum to the manufacturer, or more important how much a manufacturer would be willing to pay for gypsum from a source such as a power plant. Except for isolated cases where the power plant producing gypsum is located reasonably close to a gypsum manufacturer who would normally have to receive the material from a distant source, the selling price of the gypsum would probably be only a dollar or two a ton. Further, the acceptance of "power-plant" gypsum would be questionable, because although it may be purer than the natural product, its hardness, size, and processing qualities would be different and the manufacturing processes and/or equipment would probably have to be modified to use it. For these reasons it was decided that the lime process would be treated as a simplified system which involved no product recovery. This plan was not carried to completion, however, since other NAPCA investigators were giving adequate study to processes utilizing lime and limestone. A Case 3 analysis for the Simplified Lime Process was conducted, however, which is presented later.

B. ZINC OXIDE PROCESS

1. Process Design

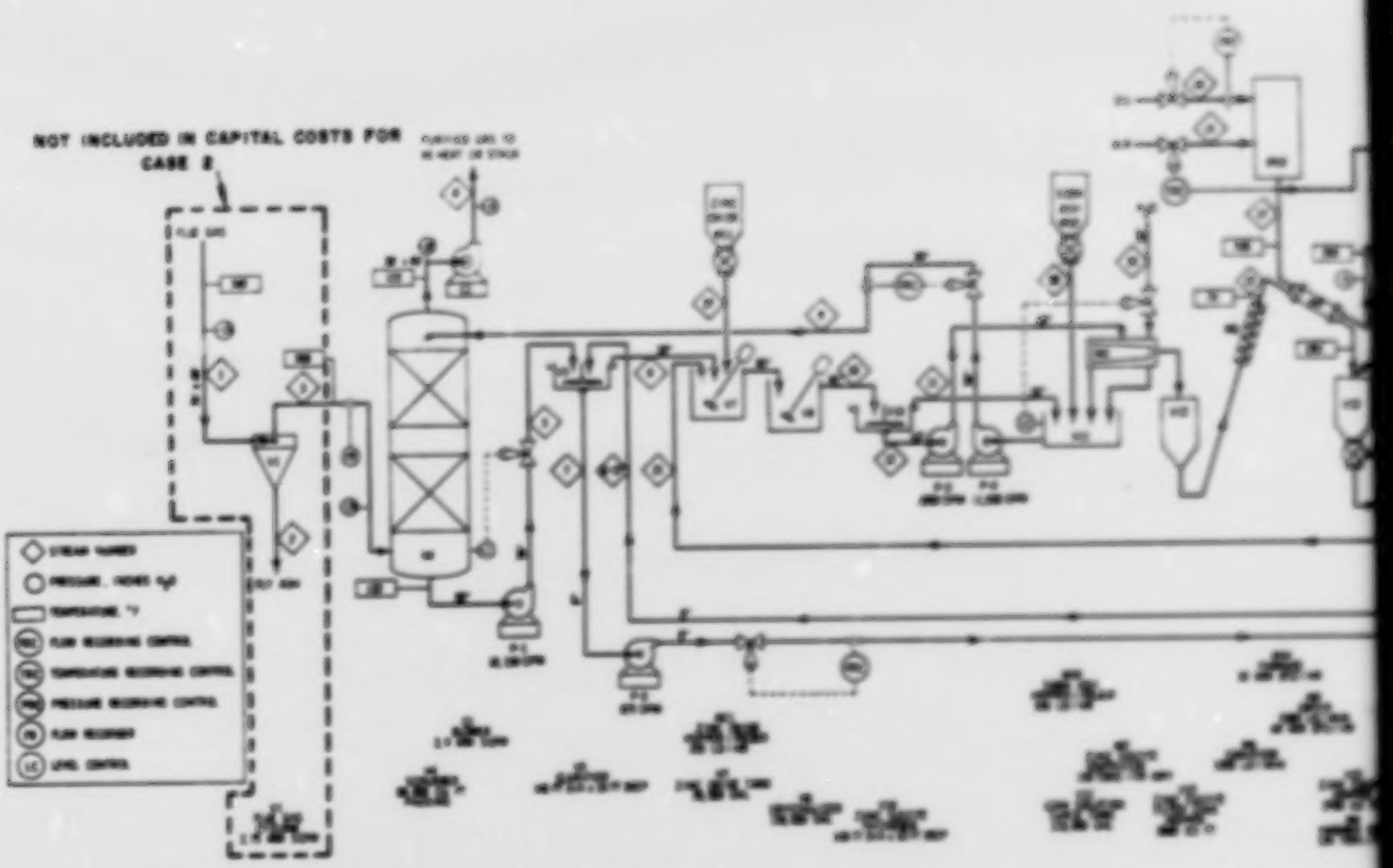
The same basic process design was used for all cases of the Zinc Oxide Process. This consisted of the original work by Johnstone, et al.,[221] and on data developed by the Bureau of Mines.[621] A departure from the design used in Cases 1, 2, and 3 was made in Case 4 which involved dust removal. A prescrubber has been substituted in Case 4 for the dry cyclone used previously. The prescrubber selected was assumed to absorb all of the H_2SO_4 and remove 95% of the dust in the smelter gas. Material balances and flow diagrams were prepared. All major equipment was sized and specifications were written. The process flow diagrams indicate the entire processing sequence and include equipment sizing information, flows, temperatures, and pressures. Tentative dimensions are given for pipe diameters, in inches, and duct work, in feet. These dimensions are based on liquid flows of 5.5 ft/sec or less and gas flows of 50 ft/sec or less. Raw material and utility requirements were estimated. The process flow diagrams are shown in Figures 45-47.

2. Capital Costs

The capital cost estimates provided the following investment requirements:

Case	Total Investment, $	$/kw Capacity
1	15,688,700	11.21
2	12,435,600	8.88
3	3,510,000	15.95
4	9,213,500	—

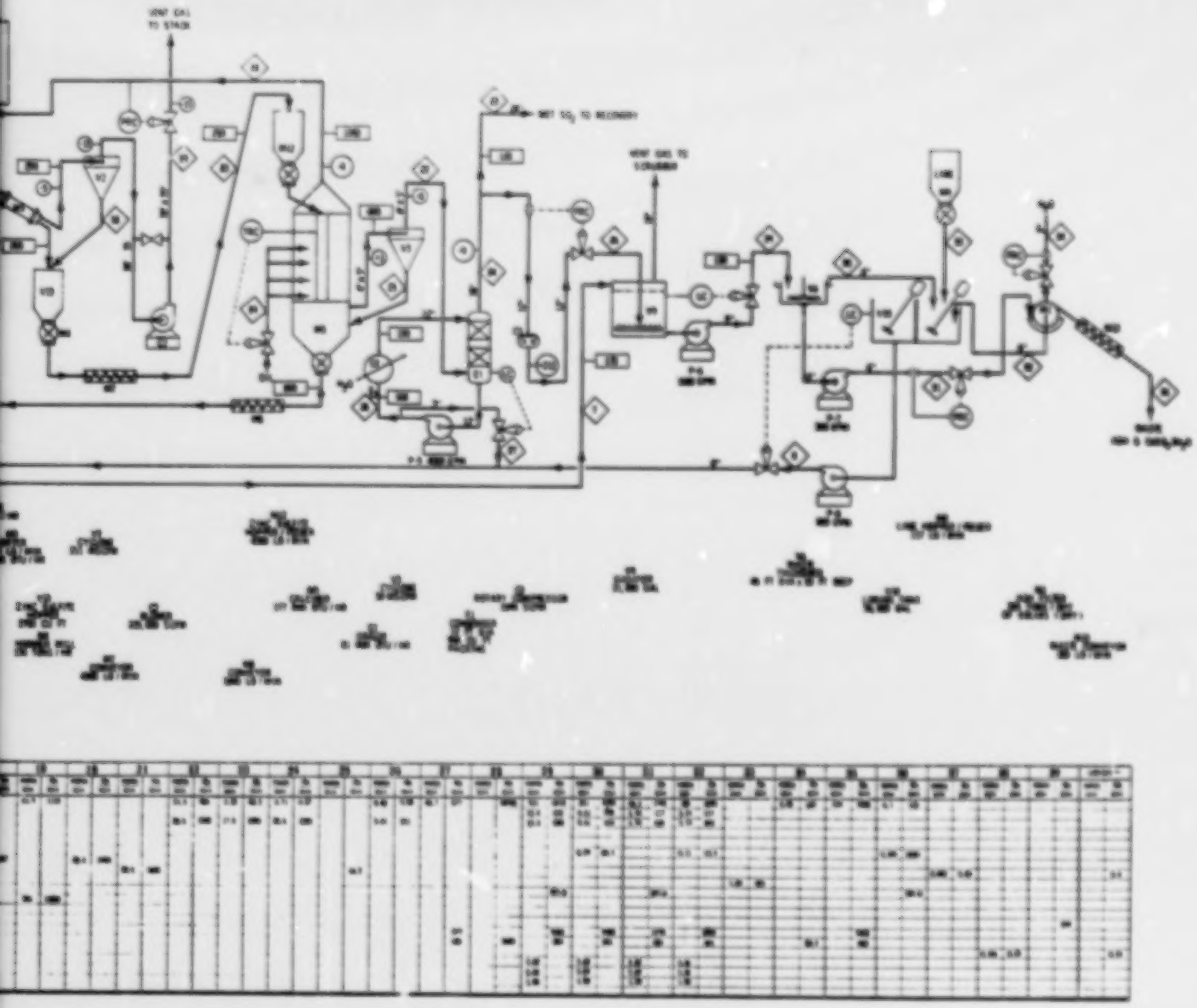
Capital cost estimate summaries are presented for each case (see Tables 76-79). Equipment lists showing basic data and individual equipment estimated costs are in Appendix C. The equipment list for Cases 1 and 2 is identical except that the flue gas cyclone is considered to be a part of existing power plant equipment in Case 2. Derivation of working capital is shown in Tables 80-83.


NOT INCLUDED IN CAPITAL COSTS FOR
CASE 2

ZINC OXIDE PROCESS

CASE 1 - 1400 MEGAWATT NEW

CASE 2 - 1400 MEGAWATT EXIST


VENT GAS TO STACK
WET SO2 TO RECOVERY
VENT GAS TO SCRUBBER
LIME

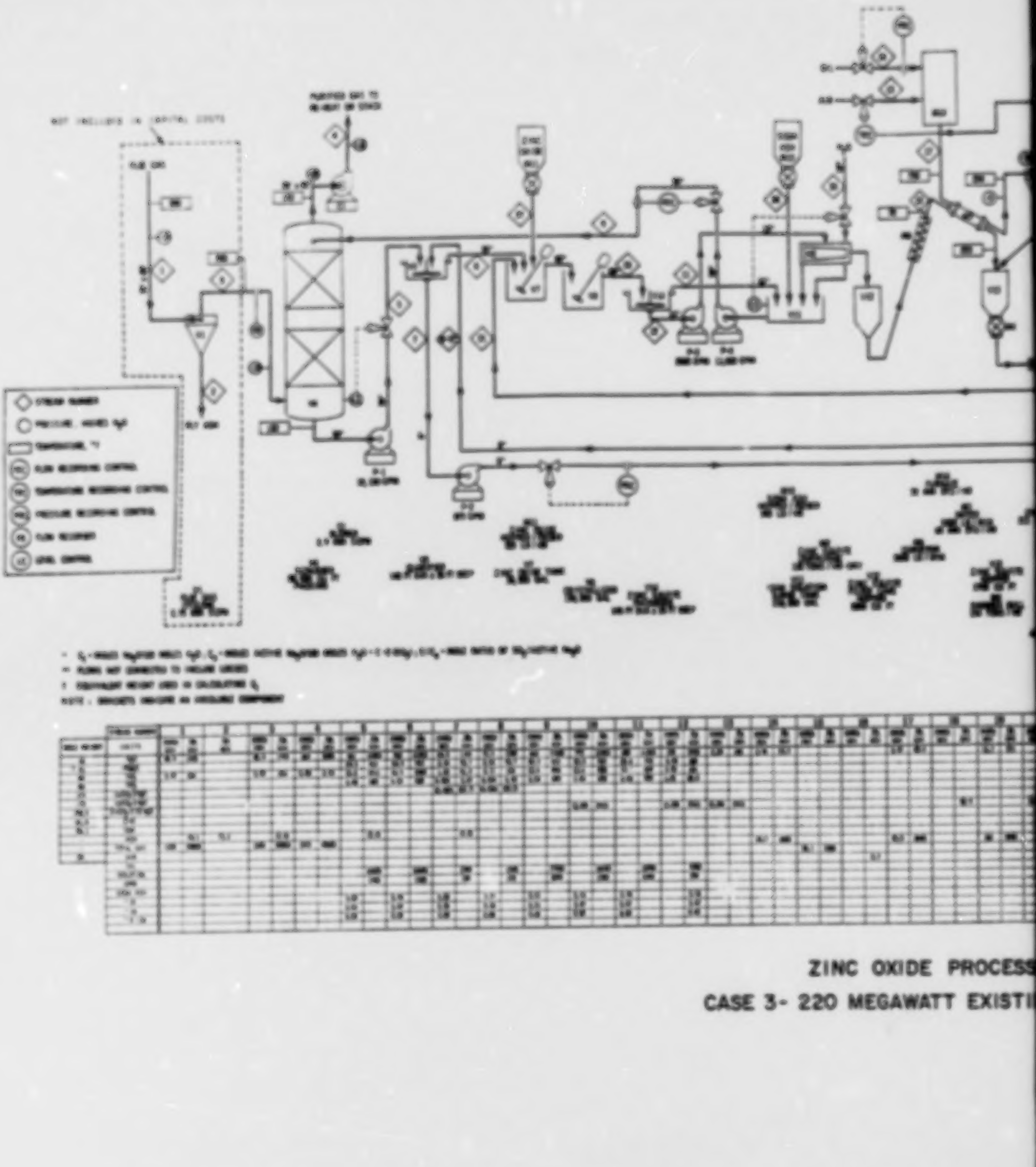
CESS FLOW DIAGRAM

NEW POWER PLANT FACILITY

EXISTING POWER PLANT FACILITY

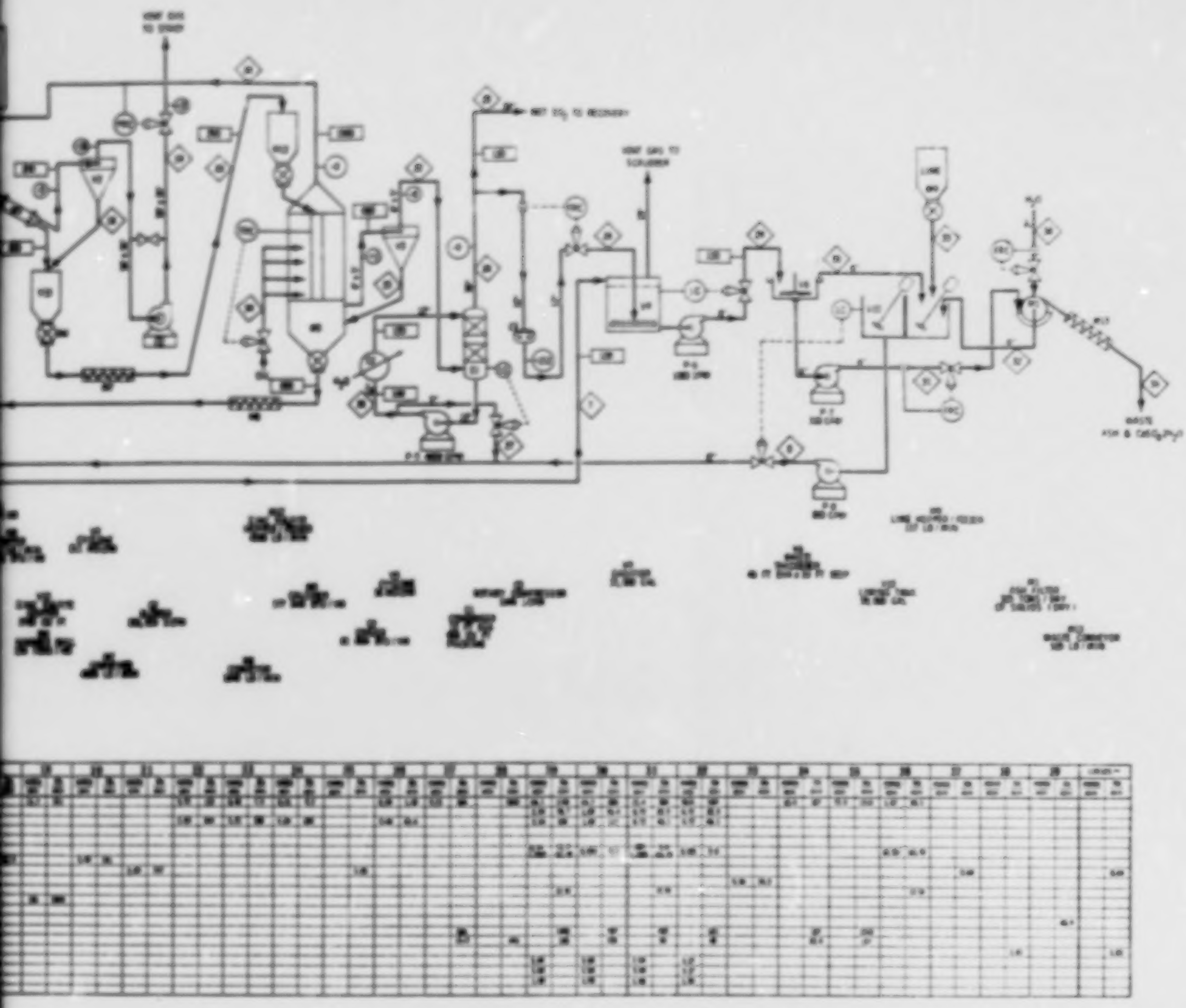
Figure 45

B


NOT INCLUDED IN CAPITAL COSTS
FLUE GAS
STREAM NUMBER
PRESSURE, INCHES H₂O
TEMPERATURE, °F
FLOW RECORDING CONTROL
TEMPERATURE RECORDING CONTROL
PRESSURE RECORDING CONTROL
FLOW RECORDER
LEVEL CONTROL

ZINC OXIDE PROCESS

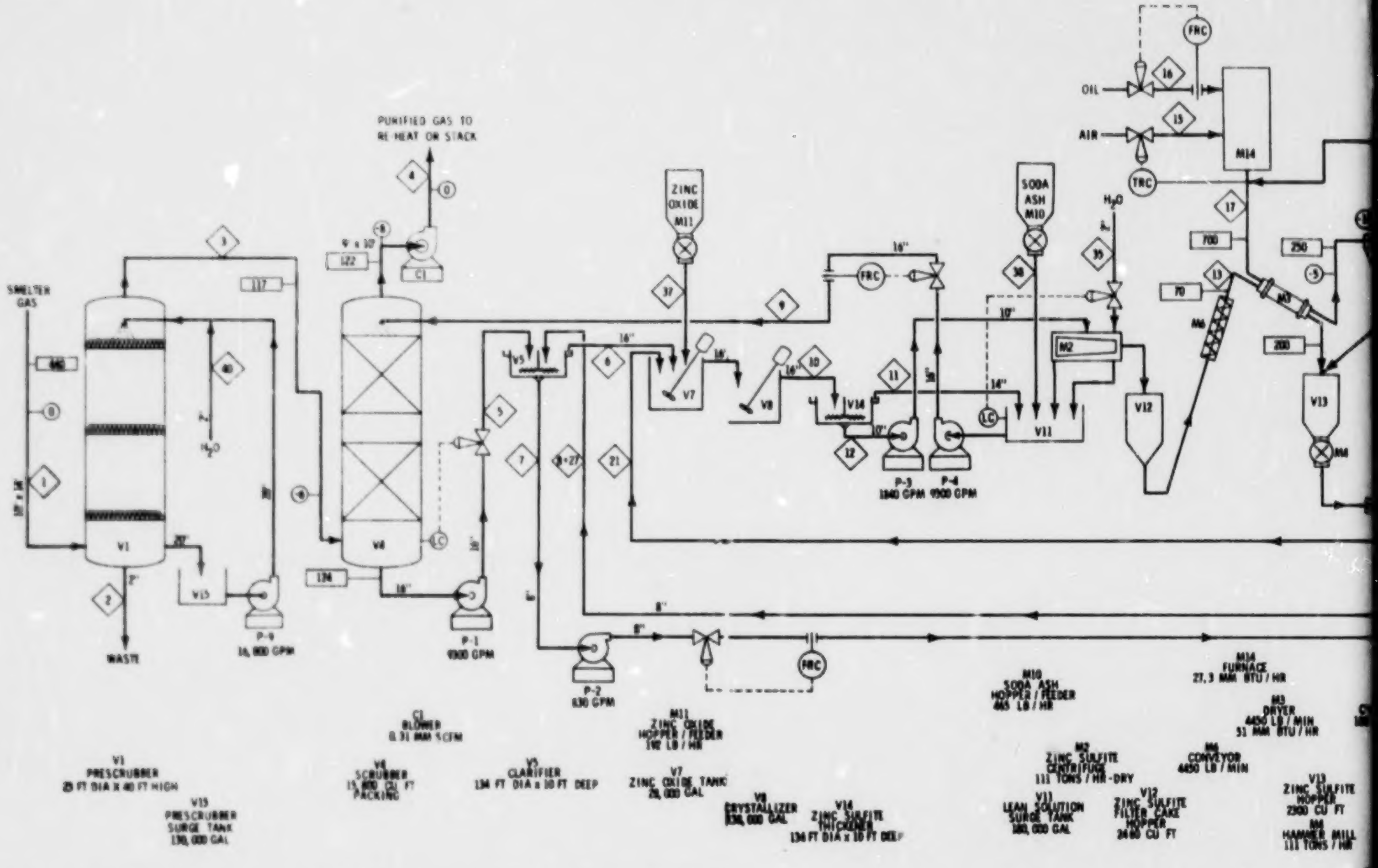
CASE 3- 220 MEGAWATT EXISTI


VENT GAS TO STACK
VENT GAS TO SCRUBBER
LIME

ROCESS FLOW DIAGRAM
EXISTING POWER PLANT FACILITY

Figure 46

B


PURIFIED GAS TO
RE HEAT OR STACK
SMELTER GAS
WASTE
V1
V15
V4
C1
9 x 10
122
117
134
P-9
16,800 GPM
P-1
6900 GPM
P-2
630 GPM
P-3
1840 GPM
P-4
6900 GPM
ZINC OXIDE
M11
SODA ASH
M10
OIL
AIR
H2O
FRC
TRC
LC
M14
M2
M3
M4
M6
V5
V7
V8
V14
V11
V12
V13
700
250
70
200
16"
14"
10"
8"
1
2
3
4
5
6
7
8
9
10
11
12
13
15
16
17
21
35
37
38
C1
BLOWER
0.31 MM SCFM
V1
PRESCRUBBER
25 FT DIA X 40 FT HIGH
V15
PRESCRUBBER
SURGE TANK
130,000 GAL
V4
SCRUBBER
15,800 CU FT
PACKING
V5
CLARIFIER
134 FT DIA x 10 FT DEEP
M11
ZINC OXIDE
HOPPER / FEEDER
192 LB / HR
V7
ZINC OXIDE TANK
28,000 GAL
V8
CRYSTALLIZER
130,000 GAL
V14
ZINC SULFITE
THICKENER
134 FT DIA x 10 FT DEEP
M10
SODA ASH
HOPPER / FEEDER
465 LB / HR
V11
LEAN SOLUTION
SURGE TANK
180,000 GAL
M2
ZINC SULFITE
CENTRIFUGE
111 TONS / HR - DRY
V12
ZINC SULFITE
FILTER CAKE
HOPPER
2480 CU FT
M6
CONVEYOR
4450 LB / MIN
M14
FURNACE
27.3 MM BTU / HR
M3
DRYER
4450 LB / MIN
51 MM BTU / HR
V13
ZINC SULFITE
HOPPER
2300 CU FT
M4
HAMMER MILL
111 TONS / HR

* C_1 = MOLES Na_2O/100 MOLES H_2O ; C_2 = MOLES ACTIVE Na_2O/100 MOLES H_2O = C_1 - 2 (SO_3) ; S/C_2 = MOLE RATIO OF SO_2/ACTIVE Na_2O

** FLOWS NOT CORRECTED TO INCLUDE LOSSES

† EQUIVALENT WEIGHT USED IN CALCULATING C_1

NOTE: BRACKETS INDICATE AN INSOLUBLE COMPONENT.

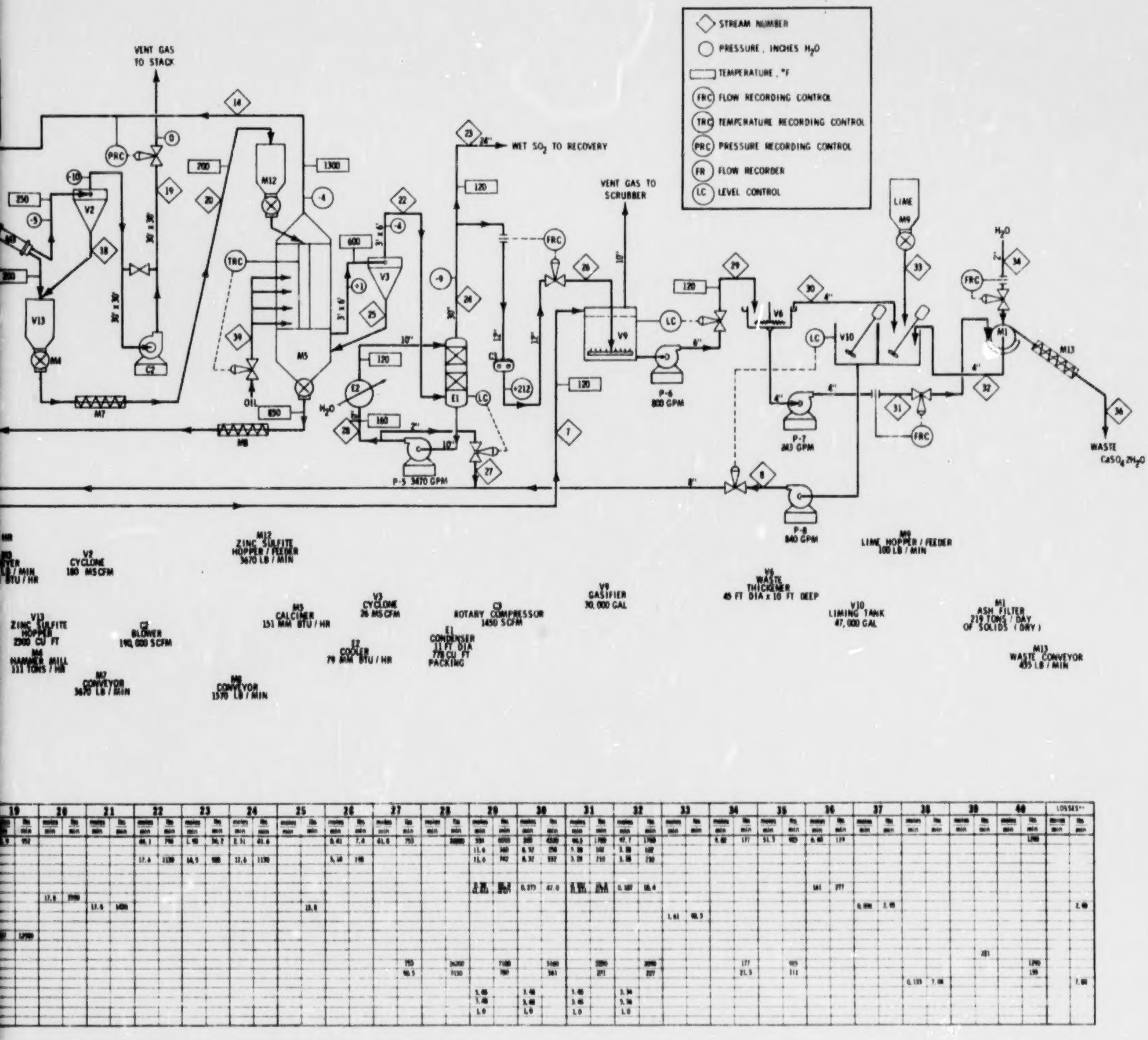
MOLE WEIGHT	STREAM NUMBER	1		2		3		4		5		6		7		8		9		10	
	UNITS	moles/min	lbs/min	moles/min	lbs/min	moles/min	lbs/min	moles/min	lbs/min	moles/min	lbs/min	moles/min	lbs/min	moles/min	lbs/min	moles/min	lbs/min	moles/min	lbs/min	moles/min	lbs/min
18	H_2O	[illegible]	[illegible]	[illegible]	12.0	71.6	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
† 31	$+Na_2O$									133	[illegible]	[illegible]	[illegible]	11.6	[illegible]	11.6	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
64	SO_2	17.0	[illegible]			17.0	[illegible]	[illegible]	[illegible]	71.2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
80	SO_3	[illegible]	[illegible]	[illegible]	[illegible]					[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
129	$CaSO_3 \cdot \frac{1}{2}H_2O$													[illegible]	[illegible]	[illegible]	[illegible]				
172	$CaSO_4 \cdot 2H_2O$																				
[illegible]	$ZnSO_3 \cdot 2\frac{1}{2}H_2O$																			[illegible]	[illegible]
81.4	ZnO																				
56.1	CaO																				
	ASH		6.0		6.0																
	TOTAL GAS	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]	[illegible]												
29	AIR																				
	OIL																				
	SOLUTION										[illegible]		[illegible]		[illegible]		[illegible]		[illegible]		[illegible]
	GPM										[illegible]		[illegible]		[illegible]		[illegible]		[illegible]		[illegible]
	SODA ASH																				
	* C_1									[illegible]		[illegible]		[illegible]		[illegible]		[illegible]		[illegible]	
	* C_2									[illegible]		[illegible]		[illegible]		[illegible]		[illegible]		[illegible]	
	* S/C_2									[illegible]		[illegible]		[illegible]		[illegible]		[illegible]		[illegible]	

MOLE WEIGHT	STREAM NUMBER	11		12		13		14		15		16		17		18		19		20	
	UNITS	moles/min	lbs/min	moles/min	lbs/min	moles/min	lbs/min	moles/min	lbs/min	moles/min	lbs/min	moles/min	lbs/min	moles/min	lbs/min	moles/min	lbs/min	moles/min	lbs/min	moles/min	
18	H_2O	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	13.4	241					13.6	[illegible]			32.9	[illegible]		
† 31	$+Na_2O$	[illegible]	[illegible]	27.9	[illegible]																
64	SO_2	45.4	[illegible]	11.5	[illegible]																
80	SO_3	18.7	[illegible]	4.50	[illegible]																
129	$CaSO_3 \cdot \frac{1}{2}H_2O$																				
172	$CaSO_4 \cdot 2H_2O$																				
[illegible]	$ZnSO_3 \cdot 2\frac{1}{2}H_2O$			17.6	[illegible]	17.6	[illegible]										137			[illegible]	[illegible]
81.4	ZnO																				
56.1	CaO																				
	ASH																				
	TOTAL GAS							[illegible]	[illegible]					[illegible]	[illegible]			[illegible]	[illegible]		
29	AIR									[illegible]	[illegible]										
	OIL												[illegible]								
	SOLUTION		[illegible]		[illegible]																
	GPM		[illegible]		[illegible]																
	SODA ASH																				
	* C_1	[illegible]		[illegible]																	
	* C_2	[illegible]		[illegible]																	
	* S/C_2	[illegible]		[illegible]																	

ZINC OXIDE PROCES

CASE 4-222,000 SCFM SMELT

A


STREAM NUMBER
PRESSURE, INCHES H_2O
TEMPERATURE, °F
FRC FLOW RECORDING CONTROL
TRC TEMPERATURE RECORDING CONTROL
PRC PRESSURE RECORDING CONTROL
FR FLOW RECORDER
LC LEVEL CONTROL
VENT GAS TO STACK
WET SO_2 TO RECOVERY
VENT GAS TO SCRUBBER
LIME
H_2O
WASTE $CaSO_4 \cdot 2H_2O$
OIL
M12 ZINC SULFITE HOPPER / FEEDER 3670 LB / MIN
V2 CYCLONE 180 MSCFM
V13 ZINC SULFITE HOPPER 2300 CU FT
M4 HAMMER MILL 111 TONS / HR
C2 BLOWER 190,000 SCFM
M7 CONVEYOR 3670 LB / MIN
M8 CONVEYOR 1570 LB / MIN
M5 CALCINER 151 MM BTU / HR
V3 CYCLONE 26 MSCFM
E2 COOLER 79 MM BTU / HR
C3 ROTARY COMPRESSOR 1450 SCFM
E1 CONDENSER 11 FT DIA 778 CU FT PACKING
P-5 3470 GPM
P-6 800 GPM
P-7 243 GPM
P-8 840 GPM
V9 GASIFIER 30,000 GAL
V6 WASTE THICKENER 45 FT DIA x 10 FT DEEP
V10 LIMING TANK 47,000 GAL
M9 LIME HOPPER / FEEDER 100 LB / MIN
M1 ASH FILTER 219 TONS / DAY OF SOLIDS (DRY)
M13 WASTE CONVEYOR 435 LB / MIN
LOSSES**

PROCESS FLOW DIAGRAM

SMELTER GAS CONTAINING 2.9% SO_2

Figure 47

TABLE 76

ZINC OXIDE PROCESS: CAPITAL COST ESTIMATE SUMMARY

Case 1

	ITEM	COST - $
1.	Purchased Equipment	3,675,000
2.	Erection Labor	918,800
3.	Foundations and Platforms	661,500
4.	Piping	1,837,500
5.	Instruments	367,500
6.	Insulation	294,000
7.	Electrical	367,500
8.	Process Buildings, Structures	918,800
9.	Plant Facilities, 5% of 1-8	452,000
10.	Plant Utilities, 7% of 1-9	664,500
11.	PHYSICAL PLANT COST	10,157,100
12.	Engineering & Construction, 20% of 11	2,031,400
13.	DIRECT PLANT COST	12,188,500
14.	Contingency, 15% of 13	1,828,300
15.	Contractor's Fee, 5% of 13 + 14	700,800
16.	FIXED CAPITAL COST	14,717,600
17.	Interest During Construction, 2.5% of 16	367,900
18.	SUB-TOTAL FOR DEPRECIATION	15,085,500
19.	Working Capital	603,200
20.	TOTAL INVESTMENT	15,688,700

21. CAPITAL REQUIREMENTS: \$ 11.21 /kw capacity

TABLE 78

ZINC OXIDE PROCESS: CAPITAL COST ESTIMATE SUMMARY

Case 3

	ITEM	COST - $
1.	Purchased Equipment	815,000
2.	Erection Labor	203,800
3.	Foundations and Platforms	146,700
4.	Piping	407,500
5.	Instruments	81,500
6.	Insulation	65,200
7.	Electrical	81,500
8.	Process Buildings, Structures	203,800
9.	Plant Facilities, 5% of 1-8	100,300
10.	Plant Utilities, 7% of 1-9	147,400
11.	PHYSICAL PLANT COST	2,252,700
12.	Engineering & Construction, 20% of 11	450,500
13.	DIRECT PLANT COST	2,703,200
14.	Contingency, 15% of 13	405,500
15.	Contractor's Fee, 5% of 13 + 14	155,400
16.	FIXED CAPITAL COST	3,264,100
17.	Interest During Construction, 2.5% of 16	81,600
18.	SUB-TOTAL FOR DEPRECIATION	3,345,700
19.	Working Capital	168,500
20.	TOTAL INVESTMENT	3,514,200

21. CAPITAL REQUIREMENTS: $ 15.97 /kw capacity

TABLE 79

ZINC OXIDE PROCESS: CAPITAL COST ESTIMATE SUMMARY

Case 4

	ITEM	COST - $
1.	Purchased Equipment	2,140,000
2.	Erection Labor	535,000
3.	Foundations and Platforms	385,200
4.	Piping	1,070,000
5.	Instruments	214,000
6.	Insulation	171,200
7.	Electrical	214,000
8.	Process Buildings, Structures	535,000
9.	Plant Facilities, 5% of 1-8	263,200
10.	Plant Utilities, 7% of 1-9	386,900
11.	PHYSICAL PLANT COST	5,914,500
12.	Engineering & Construction, 20% of 11	1,182,900
13.	DIRECT PLANT COST	7,097,400
14.	Contingency, 15% of 13	1,064,600
15.	Contractor's Fee, 5% of 13 + 14	408,100
16.	FIXED CAPITAL COST	8,570,100
17.	Interest During Construction, 2.5% of 16	214,300
18.	SUB-TOTAL FOR DEPRECIATION	8,784,400
19.	Working Capital	460,000
20.	TOTAL INVESTMENT	9,213,500

TABLE 80

ZINC OXIDE PROCESS: WORKING CAPITAL

Case 1

70% Plant Factor

	COST - $		
	ZnO	H_2SO_4	Plume Reheat
Raw Material Inventory, 2 months	98,100	-	-
Direct Labor, 3 months	32,100	24,700	-
Maintenance, 3 months	110,400	50,000	1,500
Supplies, 3 months	22,100	10,000	300
Payroll Burden, 3 months	6,800	5,300	-
Plant Overhead, 4 months	112,900	58,900	1,200
Fixed Cost, 0.5% fixed capital cost	73,600	20,000	1,000
Spare Parts & Miscellaneous, 1.0% fixed capital cost	147,200	40,000	2,000
Sub-total:	603,200	208,900	6,000

Total: $818,100

TABLE 81

ZINC OXIDE PROCESS: WORKING CAPITAL

Case 2

70% Plant Factor

	COST - $		
	ZnO	H_2SO_4	Plume Reheat
Raw Material Inventory, 2 months	98,100	-	-
Direct Labor, 3 months	32,100	24,700	-
Maintenance, 3 months	87,300	50,000	1,500
Supplies, 3 months	17,500	10,000	300
Payroll Burden, 3 months	6,800	5,300	-
Plant Overhead, 4 months	94,400	58,900	1,200
Fixed Cost, 0.5% fixed capital cost	58,200	20,000	1,000
Spare Parts & Miscellaneous, 1.0% fixed capital cost	116,300	40,000	2,000
Sub-total:	510,700	208,900	6,000
Total:	$725,600		

TABLE 82

ZINC OXIDE PROCESS: WORKING CAPITAL

Case 3

70% Plant Factor

	COST - $		
	ZnO	H_2SO_4	Plume Reheat
Raw Material Inventory, 2 months	18,900	-	-
Direct Labor, 3 months	26,100	24,700	
Maintenance, 3 months	24,500	16,500	500
Supplies, 3 months	4,900	3,300	100
Payroll Burden, 3 months	5,600	5,300	-
Plant Overhead, 4 months	39,600	32,100	400
Fixed Cost, 0.5% fixed capital cost	16,300	6,600	400
Spare Parts & Miscellaneous, 1.0% fixed capital cost	32,600	13,200	700
Sub-total:	168,500	101,700	2,100

Total: $272,300

TABLE 83

ZINC OXIDE PROCESS: WORKING CAPITAL

Case 4

90% Plant Factor

	COST - $		
	ZnO	H_2SO_4	Plume Reheat
Raw Material Inventory, 2 months	139,200	-	-
Direct Labor, 3 months	32,100	$24,700	-
Maintenance, 3 months	64,300	45,000	$400
Supplies, 3 months	12,900	9,000	100
Payroll Burden, 3 months	6,800	6,800	-
Plant Overhead, 4 months	76,100	54,900	300
Fixed Cost, 0.5% fixed capital cost	42,900	18,000	200
Spare Parts & Miscellaneous, 1.0% fixed capital cost	85,700	36,000	500
Sub-total	460,000	194,400	1,500
TOTAL:	$655,900		

3. Operating Costs

The initial economic analyses of the cases evaluated in Phase III assumed a 90% plant factor (330 days operation per year). In Cases 1, 2 and 4 operations were considered to be continuous under these conditions. In Case 3, however, operations averaged 60% of capacity on the operating days, equivalent to a 54% plant factor. In all cases a plume reheat of 50°F (a rise from 122° to 172°F) was used.

Some of the guidelines for operations of SO_2 recovery systems in conjunction with power plants were changed by NAPCA[*] after this work was completed. It was decided that the 90% plant factor was much too high for most power plant operations due to the wide fluctuations in power load created by the variable demand for power. A decision was made to use a 70% plant factor in these cases. It was also decided to standardize on the plume reheat temperature. This is now set at a plume temperature of 200°F minimum and at least 50°F above the exit gas dewpoint.

The estimated operating costs in accordance with the new guidelines are presented below. These costs do not include by-product credits. The effect of sulfuric acid sales on these costs is discussed in the next section.

Case 1

System	M$/year	$/ton coal	mill/kwh
ZnO Process	5,082	1.43	0.59
Plume Reheat	502	0.14	0.06
Sulfuric Acid	1,745	0.49	0.20
Total	7,329	2.06	0.85

Case 2

System	M$/year	$/ton coal	mill/kwh
ZnO Process	4,473	1.26	0.52
Plume Reheat	502	0.14	0.06
Sulfuric Acid	1,745	0.49	0.20
Total	6,720	1.89	0.78

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[*] NAPCA Contractors' Meeting, Cincinnati, Ohio on December 12, 1968.

Case 3

System	M$/year	$/ton coal	mill/kwh
ZnO Process	1,225	2.22	0.91
Plume Reheat	106	0.19	0.08
Sulfuric Acid	618	1.12	0.46
Total	1,949	3.53	1.45

Case 4

System	M$/year	$/ton coal	mill/kwh
ZnO Process	3,970	–	–
Plume Reheat	50	–	–
Sulfuric Acid	1,714	–	–
Total	5,734	–	–

A 90% plant factor was used in Case 4 since the operations of a smelter facility would not be subject to the load fluctuations experienced in power plant operations.

Operating cost summary sheets are presented for Cases 1-4 according to the new guidelines in Tables 84-87. Individual operating cost data sheets are presented for the plume reheat facility and sulfuric acid plants as Tables 88-93. Detail sheets for each case show the raw material requirements and costs, manning table and costs, and utility requirements and costs. These data are presented in Tables 94-102.

Raw material requirements were obtained from material balance data shown on the flow diagrams. Raw material purities have been accounted for in the estimate of their usage. In-plant loss allowances were selected on the basis of total usage, i.e., 0.2% for solid materials (ZnO and lime) and 0.1% of the absorbing liquid (Na_2O equivalent). The raw material requirement tables indicate a substantial reduction in raw material cost if limestone could be substituted for lime. The use of limestone apparently has not been tried in this process.

The manning table shows the direct labor requirement for each cost center.

TABLE 84

ZINC OXIDE PROCESS: OPERATING COST ESTIMATE SUMMARY

Case 1

70% Plant Factor

Fixed Capital Cost: $14,717,600

	ITEM	TOTAL $	%
1.	Raw Materials & Chemicals	588,400	11.58
2.	Direct Labor	128,500	2.53
3.	Supervision, 15% of 2	19,300	0.38
4.	Maintenance, 3% of fixed capital cost	441,500	8.69
5.	Supplies, 20% of 4	88,300	1.74
6.	Utilities	1,277,000	25.12
7.	Other	-	-
8.	TOTAL DIRECT COST	2,543,000	50.04
9.	Payroll Burden, 18.5% of 2 & 3	27,300	0.54
10.	Plant Overhead, 50% of 2, 3, 4 & 5	338,800	6.67
11.	Waste Disposal	61,100	1.20
12.	Other	-	-
13.	TOTAL INDIRECT COST	427,200	8.41
14.	Depreciation, 11% depreciable capital cost	1,659,400	32.65
15.	Taxes & Insurance, 3% depreciable cap. cost	452,600	8.90
16.	Other	-	-
17.	TOTAL FIXED COST	2,112,000	41.55
18.	TOTAL OPERATING COST	5,082,200	100.0

19. Cost: $ 1.43 /ton coal, 0.59 mill/kwh

TABLE 85

ZINC OXIDE PROCESS: OPERATING COST ESTIMATE SUMMARY

Case 2

70% Plant Factor

Fixed Capital Cost: $11,634,000

ITEM	TOTAL $	%
1. Raw Materials & Chemicals	588,400	13.15
2. Direct Labor	128,500	2.87
3. Supervision, 15% of 2	19,300	0.44
4. Maintenance, 3% of fixed capital cost	349,000	7.80
5. Supplies, 20% of 4	69,800	1.56
6. Utilities	1,277,000	28.55
7. Other	-	-
8. TOTAL DIRECT COST	2,432,000	54.37
9. Payroll Burden, 18.5% of 2 & 3	27,300	0.61
10. Plant Overhead, 50% of 2, 3, 4 & 5	283,300	6.33
11. Waste Disposal	61,100	1.37
12. Other	-	-
13. TOTAL INDIRECT COST	371,700	8.31
14. Depreciation, 11% depreciable capital cost	1,311,700	29.32
15. Taxes & Insurance, 3% depreciable cap. cost	357,700	8.00
16. Other	-	-
17. TOTAL FIXED COST	1,669,400	37.32
18. TOTAL OPERATING COST	4,473,100	100.0

19. Cost: $ 1.26 /ton coal, 0.52 mill/kwh

TABLE 86

ZINC OXIDE PROCESS: OPERATING COST ESTIMATE SUMMARY

Case 3

70% Plant Factor

Fixed Capital Cost: $3,264,100

	ITEM	TOTAL $	%
1.	Raw Materials & Chemicals	113,200	9.24
2.	Direct Labor	104,400	8.52
3.	Supervision, 15% of 2	15,700	1.28
4.	Maintenance, 3% of fixed capital cost	97,900	7.99
5.	Supplies, 20% of 4	19,600	1.60
6.	Utilities	248,300	20.26
7.	Other	-	-
8.	TOTAL DIRECT COST	599,100	48.89
9.	Payroll Burden, 18.5% of 2 & 3	22,200	1.81
10.	Plant Overhead, 50% of 2, 3, 4 & 5	118,800	9.70
11.	Waste Disposal	16,800	1.37
12.	Other	-	-
13.	TOTAL INDIRECT COST	157,800	12.88
14.	Depreciation, 11% depreciable capital cost	368,000	30.03
15.	Taxes & Insurance, 3% depreciable cap. cost	100,400	8.20
16.	Other	-	-
17.	TOTAL FIXED COST	468,400	38.23
18.	TOTAL OPERATING COST	1,225,300	100.0

19. Cost: $ 2.22 /ton coal, 0.91 mill/kwh

TABLE 87

ZINC OXIDE PROCESS: OPERATING COST ESTIMATE SUMMARY

Case 4

90% Plant Factor

Fixed Capital Cost: $8,570,100

	ITEM	TOTAL $	%
1.	**Raw Materials & Chemicals**	649,700	16.36
2.	**Direct Labor**	128,500	3.24
3.	**Supervision, 15% of 2**	19,300	0.49
4.	**Maintenance, 3% of fixed capital cost**	257,100	6.48
5.	**Supplies, 20% of 4**	51,400	1.29
6.	**Utilities**	1,319,000	33.22
7.	**Other**	-	-
8.	TOTAL DIRECT COST	2,425,000	61.08
9.	**Payroll Burden, 18.5% of 2 & 3**	27,300	0.69
10.	**Plant Overhead, 50% of 2, 3, 4 & 5**	228,200	5.75
11.	**Waste Disposal**	60,000	1.51
12.	**Other**	-	-
13.	TOTAL INDIRECT COST	315,500	7.95
14.	**Depreciation, 11% depreciable capital cost**	966,300	24.34
15.	**Taxes & Insurance, 3% depreciable cap. cost**	263,500	6.64
16.	**Other**	-	-
17.	TOTAL FIXED COST	1,229,800	30.97
18.	TOTAL OPERATING COST	3,970,300	100.0

TABLE 88

PLUME REHEAT: OPERATING COST ESTIMATE SUMMARY

122-200°F

Cases 1 & 2

70% Plant Factor

Fixed Capital Cost: $200,000

	ITEM	TOTAL $	%
1.	Raw Materials & Chemicals	-	-
2.	Direct Labor	-	-
3.	Supervision, 15% of 2	-	-
4.	Maintenance, 3% of fixed capital cost	6,000	1.20
5.	Supplies, 20% of 4	1,200	0.24
6.	Utilities	462,000	92.12
7.	Other	-	-
8.	TOTAL DIRECT COST	469,200	93.56
9.	Payroll Burden, 18.5% of 2 & 3	-	-
10.	Plant Overhead, 50% of 2, 3, 4 & 5	3,600	0.72
11.	Waste Disposal	-	-
12.	Other	-	-
13.	TOTAL INDIRECT COST	3,600	0.72
14.	Depreciation, 11% depreciable capital cost	22,600	4.50
15.	Taxes & Insurance, 3% depreciable cap. cost	6,100	1.22
16.	Other	-	-
17.	TOTAL FIXED COST	28,700	5.72
18.	TOTAL OPERATING COST	501,500	100.0

19. Cost: $ 0.141 /ton coal, 0.058 mill/kwh

TABLE 89

PLUME REHEAT: OPERATING COST ESTIMATE SUMMARY

122-200°F

Case 3

70% Plant Factor

Fixed Capital Cost: $70,000

	ITEM	TOTAL $	%
1.	Raw Materials & Chemicals	-	-
2.	Direct Labor	-	-
3.	Supervision, 15% of 2	-	-
4.	Maintenance, 3% of fixed capital cost	2,100	1.98
5.	Supplies, 20% of 4	400	0.38
6.	Utilities	92,400	86.92
7.	Other	-	-
8.	TOTAL DIRECT COST	94,900	89.28
9.	Payroll Burden, 18.5% of 2 & 3	-	-
10.	Plant Overhead, 50% of 2, 3, 4 & 5	1,300	1.22
11.	Waste Disposal	-	-
12.	Other	-	-
13.	TOTAL INDIRECT COST	1,300	1.22
14.	Depreciation, 11% depreciable capital cost	7,900	7.43
15.	Taxes & Insurance, 3% depreciable cap. cost	2,200	2.07
16.	Other	-	-
17.	TOTAL FIXED COST	10,100	9.50
18.	TOTAL OPERATING COST	106,300	100.0

19. Cost: $ 0.19 /ton coal, 0.079 mill/kwh

TABLE 90

PLUME REHEAT: OPERATING COST ESTIMATE SUMMARY

122-200°F

Case 4

90% Plant Factor

Fixed Capital Cost: $45,000

	ITEM	TOTAL $	%
1.	**Raw Materials & Chemicals**	-	-
2.	**Direct Labor**	-	-
3.	**Supervision, 15% of 2**	-	-
4.	**Maintenance, 3% of fixed capital cost**	1,400	2.79
5.	**Supplies, 20% of 4**	300	0.60
6.	**Utilities**	41,000	81.84
7.	**Other**	-	-
8.	**TOTAL DIRECT COST**	42,700	85.23
9.	**Payroll Burden, 18.5% of 2 & 3**	-	-
10.	**Plant Overhead, 50% of 2, 3, 4 & 5**	900	1.80
11.	**Waste Disposal**	-	-
12.	**Other**	-	-
13.	**TOTAL INDIRECT COST**	900	1.80
14.	**Depreciation, 11% depreciable capital cost**	5,100	10.18
15.	**Taxes & Insurance, 3% depreciable cap. cost**	1,400	2.79
16.	**Other**	-	-
17.	**TOTAL FIXED COST**	6,500	12.97
18.	**TOTAL OPERATING COST**	50,100	100.0

TABLE 91

SULFURIC ACID PLANT: OPERATING COST ESTIMATE SUMMARY

Cases 1 & 2

70% Plant Factor

Fixed Capital Cost: $4,000,000

	ITEM	TOTAL $	%
1.	Raw Materials & Chemicals	-0-	-
2.	Direct Labor	98,600	5.65
3.	Supervision, 15% of 2	14,800	0.85
4.	Maintenance, 3% of fixed capital cost	200,000	11.46
5.	Supplies, 20% of 4	40,000	2.29
6.	Utilities	619,500	35.52
7.	Other	-	-
8.	TOTAL DIRECT COST	972,900	55.77
9.	Payroll Burden, 18.5% of 2 & 3	21,000	1.20
10.	Plant Overhead, 50% of 2, 3, 4 & 5	176,700	10.13
11.	Waste Disposal	-	-
12.	Other	-	-
13.	TOTAL INDIRECT COST	197,700	11.33
14.	Depreciation, 11% depreciable capital cost	451,000	25.85
15.	Taxes & Insurance, 3% depreciable cap. cost	123,000	7.05
16.	Other	-	-
17.	TOTAL FIXED COST	574,000	32.90
18.	TOTAL OPERATING COST	1,744,600	100.0

19. Cost: $ 0.49 /ton coal, 0.20 mill/kwh, $5.68/ton H_2SO_4 (100%)

TABLE 92

SULFURIC ACID PLANT: OPERATING COST ESTIMATE SUMMARY

Case 3

70% Plant Factor

Fixed Capital Cost: $1,320,000

	ITEM	TOTAL $	%
1.	**Raw Materials & Chemicals**	-0-	-
2.	**Direct Labor**	98,600	15.96
3.	**Supervision, 15% of 2**	14,800	2.40
4.	**Maintenance, 3% of fixed capital cost**	66,000	10.68
5.	**Supplies, 20% of 4**	13,200	2.14
6.	**Utilities**	118,500	24.78
7.	**Other**	-	-
8.	**TOTAL DIRECT COST**	311,100	50.36
9.	**Payroll Burden, 18.5% of 2 & 3**	21,000	3.40
10.	**Plant Overhead, 50% of 2, 3, 4 & 5**	96,300	15.59
11.	**Waste Disposal**	-	-
12.	**Other**	-	-
13.	**TOTAL INDIRECT COST**	117,300	18.99
14.	**Depreciation, 11% depreciable capital cost**	148,800	24.09
15.	**Taxes & Insurance, 3% depreciable cap. cost**	40,600	6.56
16.	**Other**	-	-
17.	**TOTAL FIXED COST**	189,400	30.65
18.	**TOTAL OPERATING COST**	617,800	100.0

19. **Cost: $** 1.12 **/ton coal,** 0.46 **mill/kwh**, $10.71/ton H_2SO_4 (100%)

TABLE 93

SULFURIC ACID PLANT: OPERATING COST ESTIMATE SUMMARY

Case 4

90% Plant Factor

Fixed Capital Cost: $3,600,000

	ITEM	TOTAL $	%
1.	**Raw Materials & Chemicals**	-	-
2.	**Direct Labor**	98,600	5.75
3.	**Supervision, 15% of 2**	14,800	0.86
4.	**Maintenance, 3% of fixed capital cost**	180,000	10.52
5.	**Supplies, 20% of 4**	36,000	2.10
6.	**Utilities**	681,800	39.79
7.	**Other**	-	-
8.	**TOTAL DIRECT COST**	1,011,200	59.02
9.	**Payroll Burden, 18.5% of 2 & 3**	21,000	1.22
10.	**Plant Overhead, 50% of 2, 3, 4 & 5**	164,700	9.61
11.	**Waste Disposal**	-	-
12.	**Other**	-	-
13.	**TOTAL INDIRECT COST**	185,700	10.83
14.	**Depreciation, 11% depreciable capital cost**	405,900	23.69
15.	**Taxes & Insurance, 3% depreciable cap. cost**	110,700	6.46
16.	**Other**	-	-
17.	**TOTAL FIXED COST**	516,600	30.15
18.	**TOTAL OPERATING COST**	1,713,500	100.0

TABLE 94

ZINC OXIDE PROCESS:

ANNUAL RAW MATERIAL REQUIREMENTS AND COSTS

Cases 1 & 2

70% Plant Factor

Material	Cost $/unit	Quantity tons/year	Total Cost $/year
Zinc Oxide	0.15/lb	626	187,800
Soda Ash	32.70/ton	1,518	49,600
Lime	18/ton	19,500	351,000
		Total:	588,400

If limestone could be substituted for lime:

Limestone	2.50/ton*	35,500	88,800
		Total:	326,200

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*Includes:[640] $1.35/ton - f.o.b. mines
0.70/ton - freight
0.37/ton - grinding costs

TABLE 95

ZINC OXIDE PROCESS:

ANNUAL RAW MATERIAL REQUIREMENTS AND COSTS

Case 3

70% Plant Factor

Material	Cost $/unit	Quantity tons/year	Total Cost $/year
Zinc Oxide	0.15/lb	118	35,400
Soda Ash	32.70/ton	333	10,900
Lime	18/ton	3,716	66,900
		Total:	113,200

If limestone could be substituted for lime:

Limestone	2.50/ton*	6,670	16,700
		Total:	63,000

---

*Includes:[640] $1.35/ton - f. o. b. mines
0.70/ton - freight
0.37/ton - grinding costs

TABLE 96

ZINC OXIDE PROCESS:

ANNUAL RAW MATERIAL REQUIREMENTS AND COSTS

Case 4

90% Plant Factor

Material	Cost $/ unit	Quantity tons/year	Total Cost $/year
Zinc Oxide	0.15/lb	696	208,800
Soda Ash	32.70/ton	1673	54,700
Lime	18/ton	21,455	386,200
		Total	649,700

If limestone could be substituted for lime:

Limestone	2.50/ton*	39,025	97,600
		Total	361,100

---

* Includes: $1.35/ton - f.o.b. mines
0.70/ton - freight
0.37/ton - grinding costs

TABLE 97

ZINC OXIDE PROCESS:
MANNING TABLE AND COST
Cases 1 & 2

Operation	Manhours/day Shift No. 1	 2	 3	 Total
Absorption	8	8	8	24
Regeneration	8	8	8	24
Drying and Calcining	8	8	8	24
Desulfation	8	8	8	24
Waste Handling	8	8	8	24
Raw Materials	8	-	-	8
Total, manhours	48	40	40	128
Total, men	6	5	5	16

Cost: 128 hr/day x 365 day/yr x $2.75/hr [illegible]8,500

TABLE 98

ZINC OXIDE PROCESS:
MANNING TABLE AND COST

Case 3

	Manhours/day			
	Shift No.			
Operation	1	2	3	Total
Absorption	8	8	8	24
Regeneration & Desulfation	8	8	8	24
Drying & Calcining	8	8	8	24
Waste Handling	8	8	8	24
Raw Materials	8	-	-	8
Total, manhours	40	32	32	104
Total, men	5	4	4	13

Cost: 104 hr/day x 365 day/yr x $2.75/hr = $104,400

TABLE 99

ZINC OXIDE PROCESS:

MANNING TABLE AND COST

Case 4

Operation	Manhours/day Shift No. 1	2	3	Total
Absorption	8	8	8	24
Regeneration	8	8	8	24
Drying and Calcining	8	8	8	24
Desulfation	8	8	8	24
Waste Handling	8	8	8	24
Raw Materials	8	-	-	8
Total, manhours	48	40	40	128
Total, men	6	5	5	16

Cost: 128 hr/day x 365 day/yr x \$2.75/hr = \$128,500

TABLE 100

ZINC OXIDE PROCESS:

ANNUAL UTILITY REQUIREMENTS AND COSTS

Cases 1 & 2

70% Plant Factor

Utility	Cost $/unit	Quantity units/year	Total Cost $/year
Power	0.006/kwh	32,400,000	194,500
Raw Water	0.10/M gal	336,000	33,600
Recirculated Water	0.05/M gal	1,355,000	67,800
Fuel Oil	2.92/bbl	336,000	981,100
		Total:	$1,277,000

TABLE 101

ZINC OXIDE PROCESS: ANNUAL UTILITY REQUIREMENTS AND COSTS

Case 3

70% Plant Factor

Utility	Cost $/unit	Quantity units/year	Total Cost $/year
Power	0.006/kwh	6,888,600	41,400
Raw Water	0.10/M gal	74,300	7,400
Recirculated Water	0.05/M gal	281,200	14,100
Fuel Oil	2.92/bbl	63,500	185,400
		Total:	$248,300

TABLE 102

ZINC OXIDE PROCESS:
ANNUAL UTILITY REQUIREMENTS AND COSTS

Case 4

90% Plant Factor

Utility	Cost $/Unit	Quantity Units/Year	Total Cost $/Year
Power	**0.006/kwh**	**24,800,000**	**149,000**
Raw Water	**0.10/Mgal**	**136,000**	**14,000**
Recirculated Water	**0.05/Mgal**	**1,500,000**	**75,000**
Fuel Oil	**2.92/bbl**	**370,000**	**1,081,000**
		Total:	**1,319,000**

Power consumption was estimated from the total equipment horsepower specifications. Raw water needs were obtained from make-up requirements and estimated losses. The recirculated water is based on the cooling loads specified. Fuel oil is indicated as the source of heat for the calciner and dryer, although natural gas could be used as an alternate fuel.

4. Profitability

A summary of the economic analysis of each case is presented below. It was assumed the sulfuric acid would be sold with credits applied against operating costs. Various prices are shown for sulfuric acid. The $34/ton indicates the approximate selling price for 100% sulfuric acid in February 1968. The $23.50/ton value is an arbitrary selling price equivalent to about 70% of that price. The other sulfuric acid prices shown indicate the lowest prices at which the operations would break-even at full capacity, i.e., at 70% plant factor for Cases 1-3, and 90% plant factor for Case 4.

The data show that the Zinc Oxide Process may be economically sound under certain favorable marketing conditions when the SO_2 is converted and sold as concentrated sulfuric acid; whether the acid marketing situation will ever be so favorable as to permit operation of this SO_2 control process at near break-even conditions is doubtful.

Details of the economic analyses are presented in Tables 103-106. The data are shown as break-even charts in Figures 48-51.

Case 1

	Sulfuric Acid Sales, $/ton		
	34	24.85	23.50
Profit Before Tax			
$/ton of coal	0.76	-0-	-0-
mills/kwh	0.31	-0-	-0-
$/ton of H_2SO_4	9.15	-0-	-0-
Break-even point	43%	70%	78%

Case 2

	Sulfuric Acid Sales, \$/ton		
	34	24.85	23.50
Profit Before Tax			
\$/ton of coal	0.93	0.06	-0-
mills/kwh	0.38	0.02	-0-
\$/ton of H_2SO_4	11.22	1.61	-0-
Break-even point	37%	66%	70%

The economics of Case 2 would be at approximately the same level as in Case 1.

Case 3

	Sulfuric Acid Sales, \$/ton	
	34	23.50
Profit (loss) Before Tax		
\$/ton of coal	(0.12)	(1.19)
mills/kwh	(0.05)	(0.50)
\$/ton of H_2SO_4	(1.17)	(11.65)
Break-even point	73%	–

In Case 3, operation of the SO_2 removal system would result in a loss, even if acid could be sold at these very high prices.

Case 4

	Sulfuric Acid Sales, \$/ton		
	34	23.50	17.70
Profit Before Tax			
\$/ton of H_2SO_4	16.30	5.80	-0-
Break-even Point	33%	55%	90%

The economics of Case 4 would be more attractive than the others due to the relatively large quantity of recovered SO_2.

TABLE 103

ZINC OXIDE PROCESS: ECONOMIC ANALYSIS

Case 1

70% Plant Factor & 96% Conversion of SO_2 to SO_3

I. Capital Investment

Zinc Oxide Process	$15,085,500
Plume Reheat	205,000
Sulfuric Acid	4,100,000
Working Capital	818,100
Total Investment:	~ $20,209,000

II. Profitability

	Sulfuric Acid, $/ton		
	$34	$24.85	$23.50
Sales, M $, 295 M tons H_2SO_4	10,030	7,329	6,930
Operating Cost, M $			
Zinc Oxide Process	5,082	5,082	5,082
Plume Reheat	502	502	502
Sulfuric Acid	1,745	1,745	1,745
Total Operating Cost:	7,329	7,329	7,329
Profit Before Tax, M $	2,701	-0-	(399)
Profit After Tax, M $	1,296	-0-	-0-
Return on Total Investment A/T, %	6.4	-0-	-0-
Payout, years	5.9	-0-	-
Profit Before Tax			
$/ton of coal	0.76	-0-	-0-
mills/kwh	0.31	-0-	-0-
$/ton of H_2SO_4	9.15	-0-	-0-
Break-even Point	43%	70%	78%

TABLE 104

ZINC OXIDE PROCESS: ECONOMIC ANALYSIS

Case 2

70% Plant Factor & 96% Conversion of SO_2 to SO_3

I. **Capital Investment**

Zinc Oxide Process	$11,924,900
Plume Reheat	205,000
Sulfuric Acid	4,100,000
Working Capital	725,600
Total Investment:	~ $16,956,000

II. **Profitability**

	Sulfuric Acid, $/ton		
	$34	$23.50	$22.78
Sales, M $, 295 M tons H_2SO_4	10,030	6,930	6,720
Operating Cost, M $			
Zinc Oxide Process	4,473	4,473	4,473
Plume Reheat	502	502	502
Sulfuric Acid	1,745	1,745	1,745
Total Operating Cost:	6,720	6,720	6,720
Profit Before Tax, M $	3,310	210	-0-
Profit After Tax, M $	1,589	101	-0-
Return on Total Investment A/T, %	9.3	0.6	-0-
Payout years	5.0	9.0	9.5
Profit Before Tax			
$/ton of coal	0.93	0.06	-0-
mills/kwh	0.38	0.02	-0-
$/ton of H_2SO_4	11.22	1.61	-0-
Break-even Point	37%	66%	70%

TABLE 105

ZINC OXIDE PROCESS: ECONOMIC ANALYSIS

Case 3

70% Plant Factor & 96% Conversion of SO_2 to SO_3

I. Capital Investment

Zinc Oxide Process	\$3,345,700
Plume Reheat	71,800
Sulfuric Acid	1,354,000
Working Capital	272,300
Total Investment:	~ \$5,044,000

II. Profitability

	Sulfuric Acid, \$/ton	
	\$34	\$23.50
Sales, M \$, 55.4 M tons H_2SO_4	1,884	1,302
Operating Cost, M \$		
Zinc Oxide Process	1,225	1,225
Plume Reheat	106	106
Sulfuric Acid	618	618
Total Operating Cost:	1,949	1,949
Profit (loss) Before Tax, M \$	(65)	(647)
Profit After Tax, M \$	-0-	-0-
Return on Total Investment A/T, %	-0-	-0-
Payout, years	-	-
Profit (loss) Before Tax		
\$/ton of coal	(0.12)	(1.19)
mills/kwh	(0.05)	(0.50)
\$/ton of H_2SO_4	(1.17)	(11.65)
Break-even Point	73%	-

TABLE 106

ZINC OXIDE PROCESS: ECONOMIC ANALYSIS

Case 4

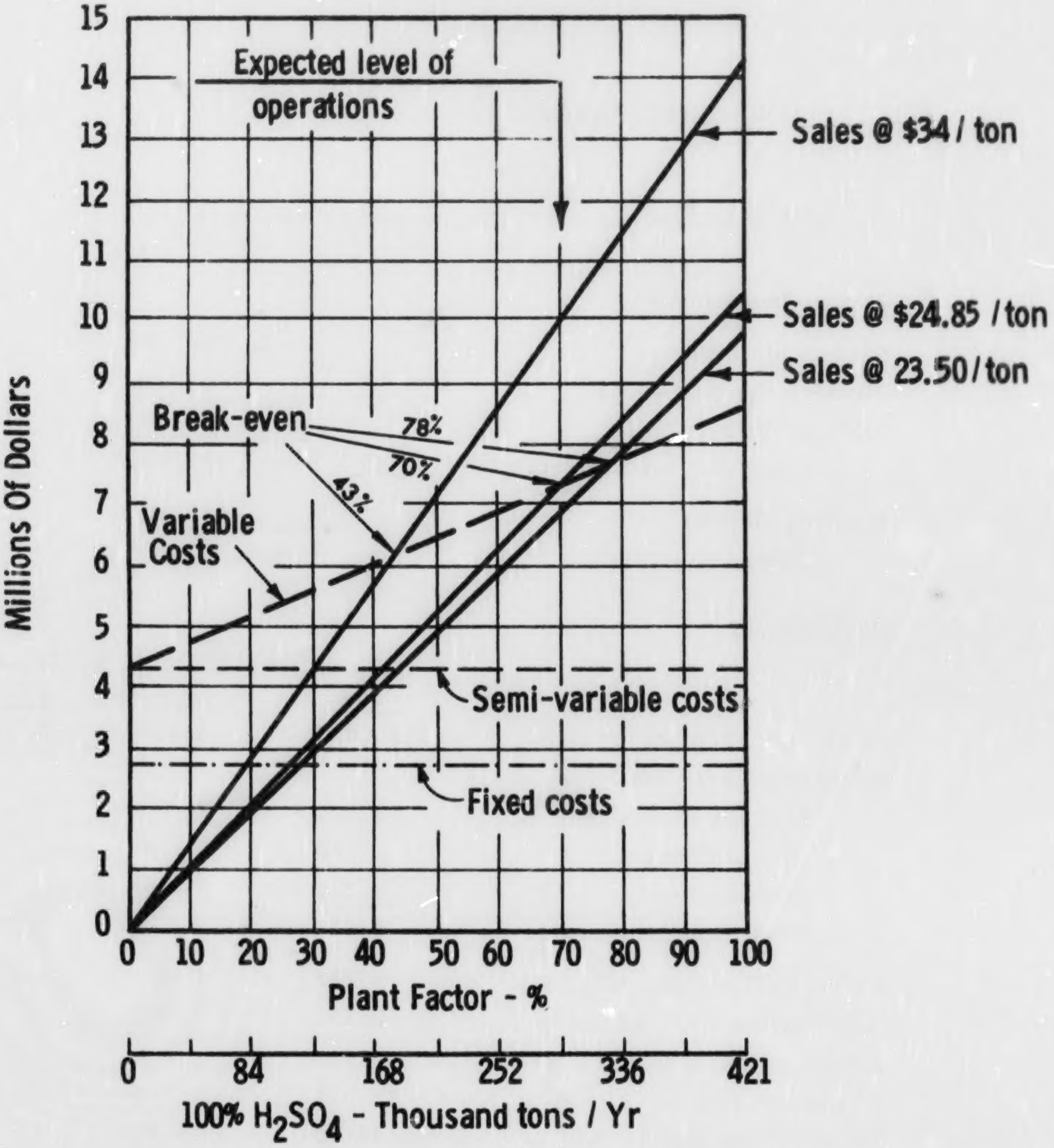
90% Plant Factor & 96% Conversion of SO_2 to SO_3

I. **Capital Investment**

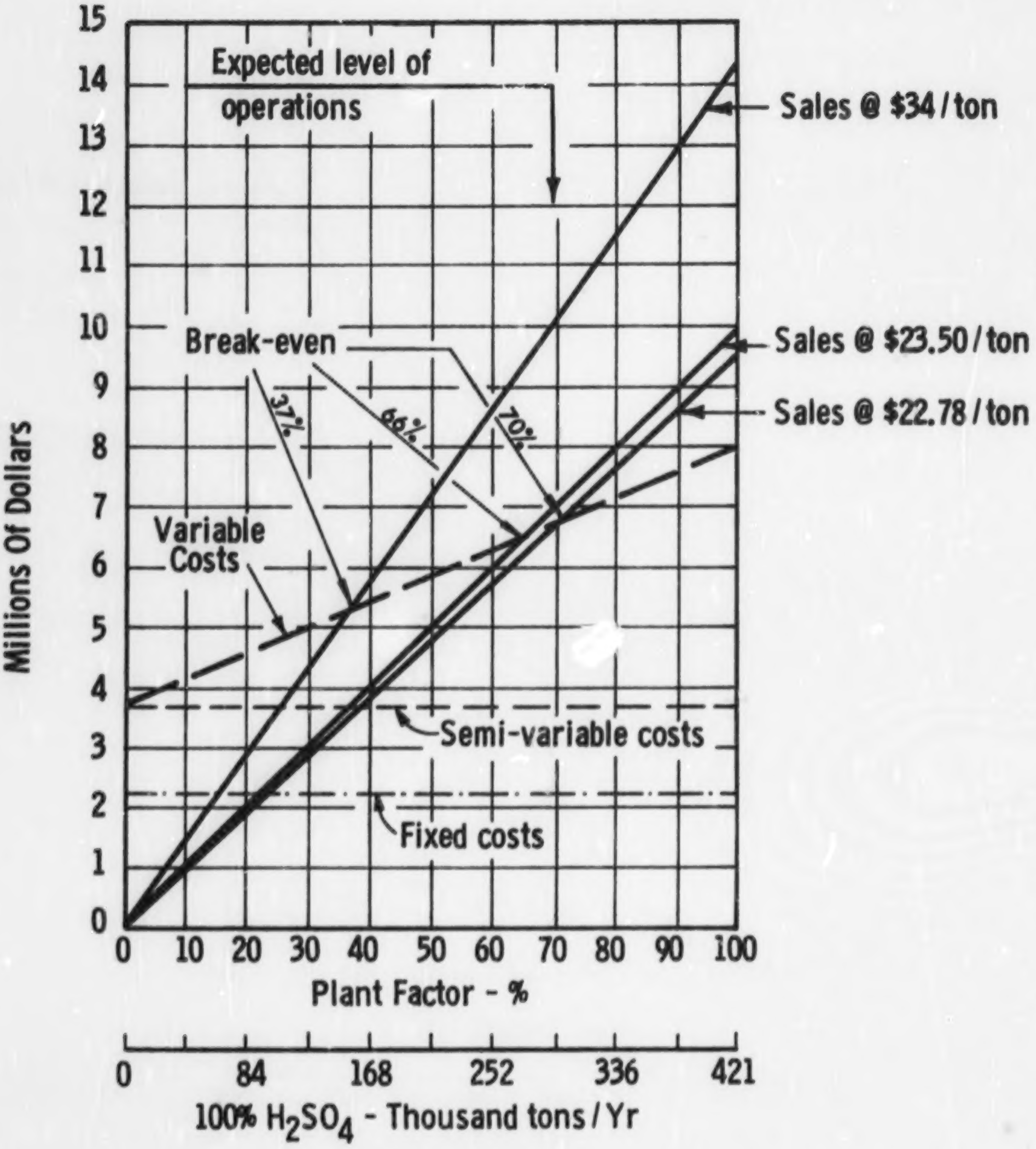
Zinc Oxide Process	**$8,784,400**
Plume Reheat to 200°F	**46,100**
Sulfuric Acid	**3,690,000**
Sub-Total for Depreciation	**$12,521,500**
Working Capital	**655,900**
Total Investment	**~ $13,177,000**

II. **Profitability**

	Sulfuric Acid, $/ton		
	$34	**$23.50**	**$17.70**
Sales, M$, 324 Mtons H_2SO_4	**11,016**	**7,614**	**5,734**
Operating Cost, M$			
Zinc Oxide Process	**3,970**	**3,970**	**3,970**
Plume Reheat	**50**	**50**	**50**
Sulfuric Acid	**1,714**	**1,714**	**1,714**
Total Operating Cost:	**5,734**	**5,734**	**5,734**
Profit Before Tax, M$	**5,282**	**1,880**	**- 0 -**
Profit After Tax, M$	**2,535**	**902**	**- 0 -**
Return on Total Investment, A/T, %	**19.2**	**6.8**	**- 0 -**
Payout, years	**3.4**	**5.8**	**9.5**
Profit, $/ton H_2SO_4, B/T	**16.30**	**5.80**	**- 0 -**
Break-even Point, %	**33**	**55**	**90**

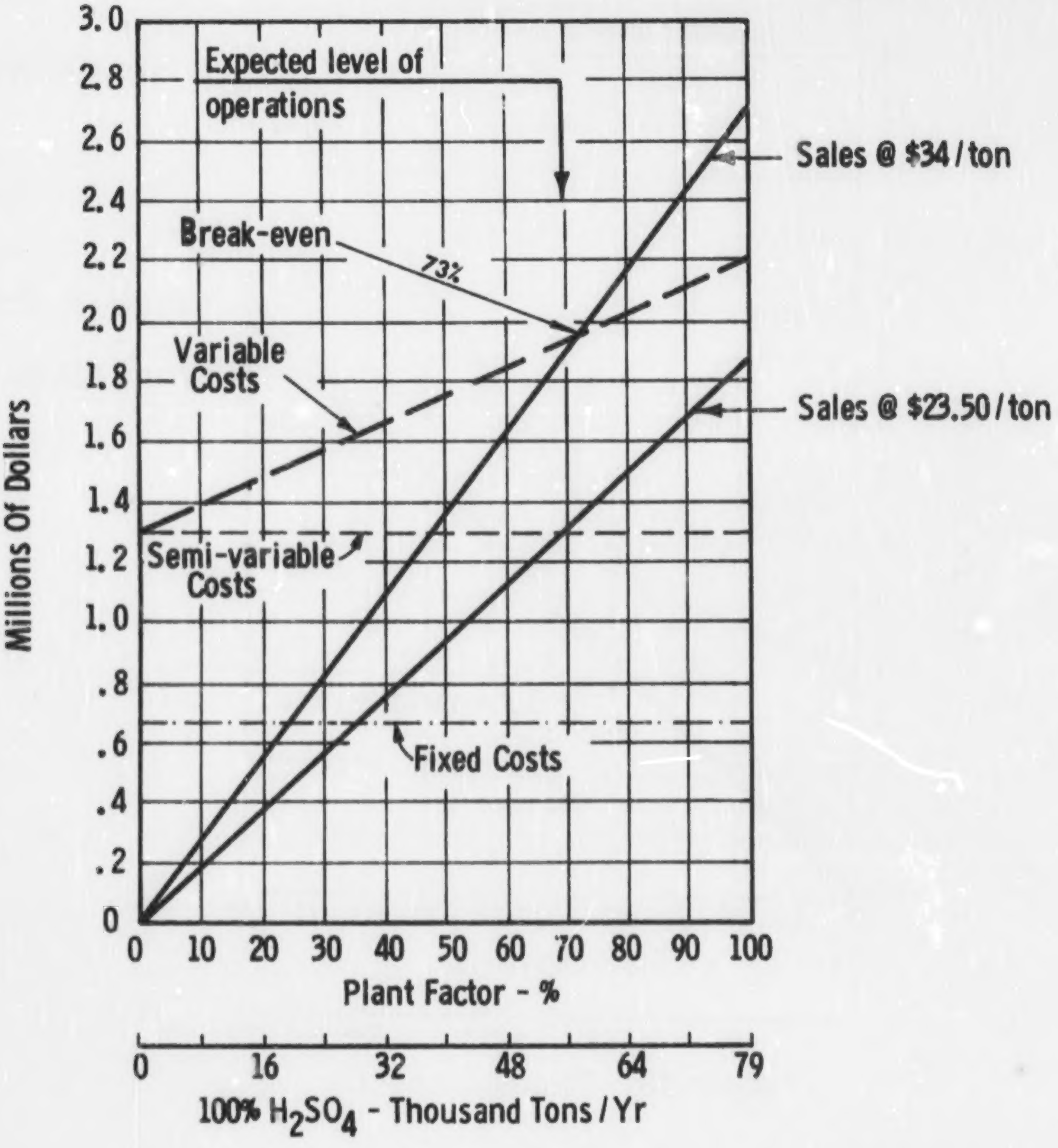


ZINC OXIDE PROCESS - CASE 1
1400 MEGAWATT NEW POWER PLANT FACILITY
BREAK-EVEN CHART WITH CONVERSION OF SO_2 TO H_2SO_4
Figure 48



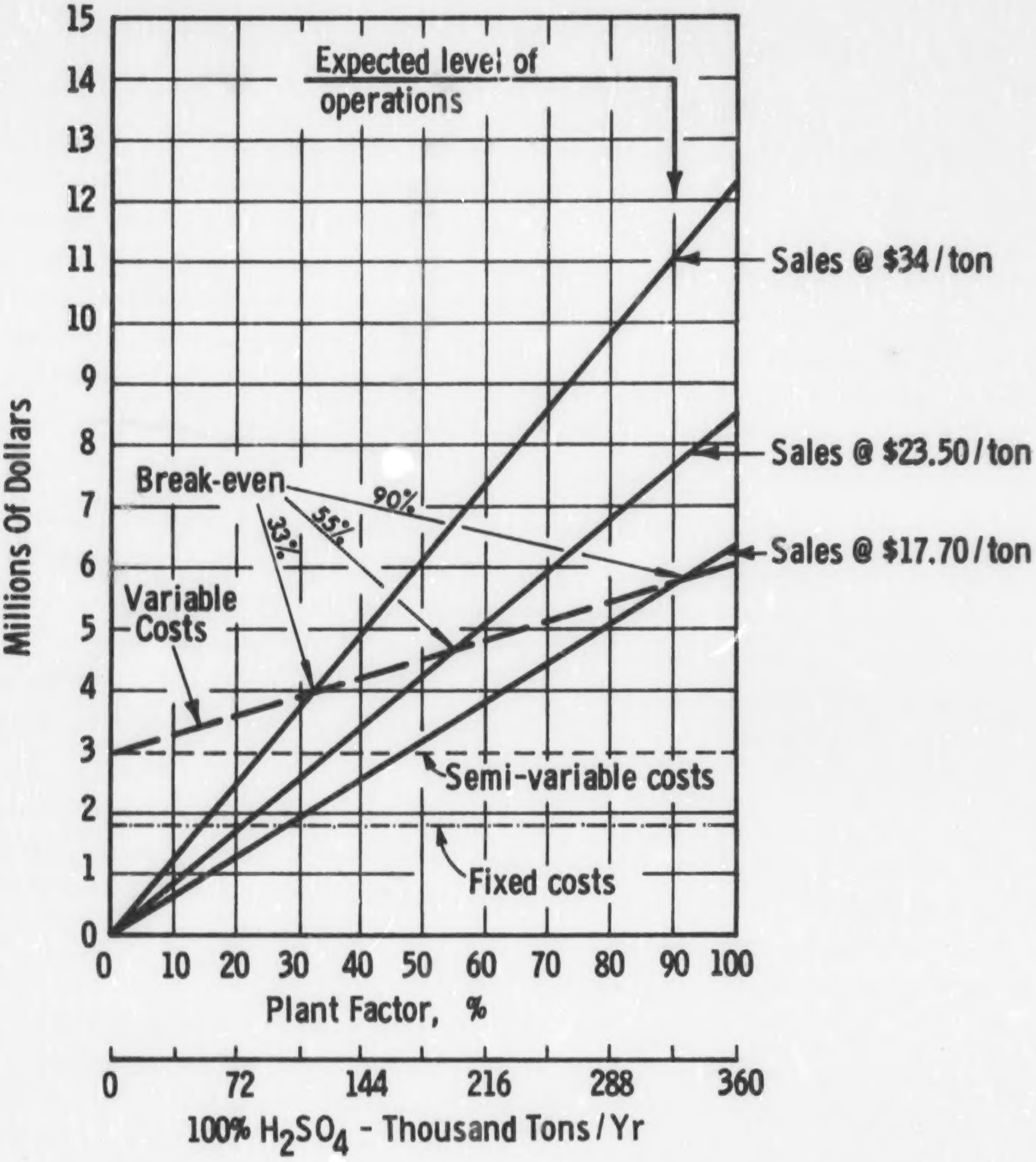
ZINC OXIDE PROCESS - CASE 2
1400 MEGAWATT EXISTING POWER PLANT FACILITY
BREAK-EVEN CHART WITH CONVERSION OF SO_2 TO H_2SO_4

Figure 49



ZINC OXIDE PROCESS - CASE 3
220 MEGAWATT EXISTING POWER PLANT FACILITY
BREAK-EVEN CHART WITH CONVERSION OF SO_2 TO H_2SO_4

Figure 50



ZINC OXIDE PROCESS - CASE 4
NEW SMELTER FACILITY
BREAK-EVEN CHART WITH CONVERSION OF SO_2 TO H_2SO_4

Figure 51

C. LIME PROCESS

1. Introduction

A reevaluation of the Mitsubishi Lime Process was made, as reported earlier, which indicated that it was probably not economic to recover gypsum as a salable by-product. For this reason it was decided that the lime process would be treated as a simplified system which involved no product recovery. This plan was not carried through to completion, however, since other NAPCA investigators are giving adequate study to processes utilizing lime and limestone. A Case 3 analysis for the Simplified Lime Process was conducted, however, and it is this work which is summarized herein.

2. Process Design

A flooded bed absorber, similar to the Turbulent Contact Absorber (TCA),* was selected as the scrubbing system for this process. This type of system consists of one or more beds in series of plastic spheres or glass marbles in turbulent motion. The motion of the spheres and their nonporous surface should prevent the accumulation of scale and thus eliminate the need for a delay tank and expensive descaling operations as described in the Howden-ICI Process.[328]

Although lime is more efficient, limestone was selected as the absorbent on the basis of cost. An excess of 35% over the theoretical was used to improve absorption.[328] A three-stage unit was specified since field tests indicated that only 80% of the SO_2 was removed from flue gas in a two-stage scrubber using limestone slurry as the absorbent.[343]

It was assumed that this system would remove 90% of the SO_2 and 98-99% of the fly ash from flue gas. The slurry, consisting of $CaCO_3$, $CaSO_4 \cdot 2H_2O$, $CaSO_3 \cdot 2H_2O$, and fly ash is circulated at a high rate. A constant make-up of $CaCO_3$ is added with the simultaneous discharge of spent slurry to a settling pond. The flow diagram, Figure 52, illustrates the system.

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* Designed and manufactured by the Air Correction Division of Universal Oil Products Company.

3. Capital Costs

The capital cost estimate, which is summarized in Table 107 indicated a total investment of $2,022,000, which is equivalent to a capital requirement of $9.19/kw capacity.

The purchased equipment cost was derived from the equipment list (Appendix C) which shows basic specifications and estimated costs. The derivation of working capital is given in Table 108.

4. Operating Costs

The operating cost at 70% plant factor was estimated at $892,000 per year, or $2.08/ton of coal, and 0.85 mill/kwh. The summary is shown in Table 109.

The only raw material required is ground limestone at a rate of 118,000 tons annually based on 98% purity and 0.2% in-plant losses.

Direct labor was based on one man per shift plus one man on day shift for raw material handling.

The electrical load was estimated at 1790 kw. Make-up water costs amount to $9,400.

No cost was charged to waste disposal, since it was assumed that adequate settling ponds would be available at the plant site.

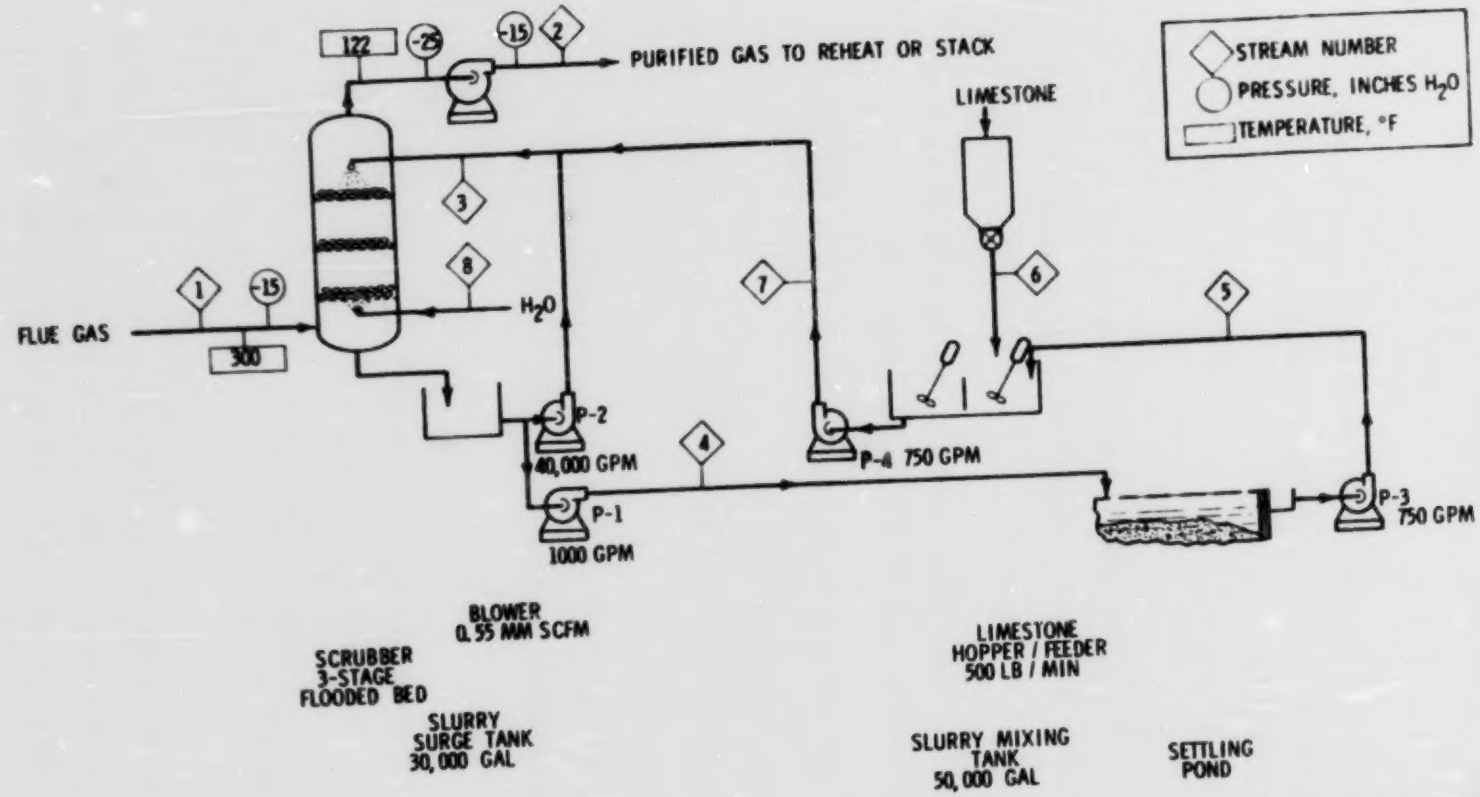
5. Profitability

A profitability analysis was not applied to this system since salable by-products are not generated.

V. RESULTS OF THE PHASE III EVALUATION

A. CAPITAL COSTS

Table 110 summarizes the total investment for each case. The capital equipment is comprised of the specific process equipment, plume reheat system, and sulfuric acid plant. The working capital is added to make up the total investment.


FLUE GAS
1
-15
300
122
-25
-15
2
PURIFIED GAS TO REHEAT OR STACK
3
8
H_2O
P-2
40,000 GPM
P-1
1000 GPM
4
7
P-4 750 GPM
LIMESTONE
6
5
P-3
750 GPM
STREAM NUMBER
PRESSURE, INCHES H_2O
TEMPERATURE, °F
BLOWER
0.55 MM SCFM
SCRUBBER
3-STAGE
FLOODED BED
SLURRY
SURGE TANK
30,000 GAL
LIMESTONE
HOPPER / FEEDER
500 LB / MIN
SLURRY MIXING
TANK
50,000 GAL
SETTLING
POND

	STREAM NUMBER	1		2		3		4		5		6		7		8		LOSSES
	UNITS	moles/min	lbs/min	moles/min	lbs/min	moles/min	lbs/min	moles/min	lbs/min	moles/min	lbs/min	moles/min	lbs/min	moles/min	lbs/min	moles/min	lbs/min	lbs/min
18	H_2O	95.9	1730	169	3050	17700	319000	389	7000	311	5600			311	5600	151	2720	
64	SO_2	3.97	254	0.40	25.4													
-	TOTAL GAS	1320	39500	1390	40600													
-	FLY ASH		79.1				3500		79.1									1.00
100	$CaCO_3$					56	5600	1.25	125			4.82	482	4.82	482			
156	$CaSO_3$ $2H_2O$					80.1	12500	1.78	278									
172	$CaSO_4$ $2H_2O$					80.2	13800	1.78	307									
-	TOTAL SOLIDS						35400		789						482			
-	SOLUTION						319000		7000		5600				5600	151	2720	
-	GPM					40000		891		672				672		327		

LIME PROCESS FLOW DIAGRAM

CASE 3-220 MEGAWATT EXISTING POWER PLANT FACILITY

Figure 52

TABLE 107

LIME PROCESS: CAPITAL COST ESTIMATE SUMMARY

Case 3

	ITEM	COST - $
1.	Purchased Equipment	468,000
2.	Erection Labor	117,000
3.	Foundations and Platforms	84,200
4.	Piping	234,000
5.	Instruments	46,800
6.	Insulation	37,400
7.	Electrical	46,800
8.	Process Buildings, Structures	117,000
9.	Plant Facilities, 5% of 1-8	57,600
10.	Plant Utilities, 7% of 1-9	84,600
11.	PHYSICAL PLANT COST .	1,293,400
12.	Engineering & Construction, 20% of 11	258,600
13.	DIRECT PLANT COST	1,552,000
14.	Contingency, 15% of 13	232,800
15.	Contractor's Fee, 5% of 13 + 14	89,200
16.	FIXED CAPITAL COST	1,874,000
17.	Interest During Construction, 2.5% of 16	47,000
18.	SUB-TOTAL FOR DEPRECIATION	1,921,000
19.	Working Capital	101,000
20.	TOTAL INVESTMENT	2,022,000

21. CAPITAL REQUIREMENTS: $ 9.19 /kw capacity

TABLE 108

LIME PROCESS: WORKING CAPITAL

Case 3

70% Plant Factor

	COST - \$
Raw Material Inventory, 2 months	28,800
Direct Labor, 3 months	8,000
Maintenance, 3 months	14,100
Supplies, 3 months	2,800
Payroll Burden, 3 months	1,700
Plant Overhead, 4 months	17,400
Fixed Cost, 0.5% fixed capital cost	9,400
Spare Parts & Miscellaneous, 1.0% fixed capital cost	18,800
TOTAL	101,000

TABLE 109

LIME PROCESS: OPERATING COST ESTIMATE SUMMARY

Case 3

70% Plant Factor

Fixed Capital Cost: $1,874,000

	ITEM	TOTAL $	%
1.	**Raw Materials & Chemicals**	381,000	42.71
2.	**Direct Labor**	32,100	3.60
3.	**Supervision, 15% of 2**	4,900	0.55
4.	**Maintenance, 3% of fixed capital cost**	56,200	6.30
5.	**Supplies, 20% of 4**	11,200	1.26
6.	**Utilities**	78,700	8.82
7.	**Other**	-	-
8.	**TOTAL DIRECT COST**	564,100	63.24
9.	**Payroll Burden, 18.5% of 2 & 3**	6,800	0.76
10.	**Plant Overhead, 50% of 2, 3, 4 & 5**	52,200	5.85
11.	**Waste Disposal**	-	-
12.	**Other**	-	-
13.	**TOTAL INDIRECT COST**	59,000	6.61
14.	**Depreciation, 11% depreciable capital cost**	211,300	23.69
15.	**Taxes & Insurance, 3% depreciable cap. cost**	57,600	6.46
16.	**Other**	-	-
17.	**TOTAL FIXED COST**	268,900	30.15
18.	**TOTAL OPERATING COST**	892,000	100.0

19. **Cost: $** 2.08 **/ton coal,** 0.85 **mill/kwh**

TABLE 110

CAPITAL INVESTMENT SUMMARY

WITH CONVERSION OF SULFUR DIOXIDE TO SULFURIC ACID

	Zinc Oxide Process				Simplified Lime Process
	Case 1	Case 2	Case 3	Case 4	Case 3
Capital Investment, Thousand $					
Process Equipment	15, 085	11, 925	3, 346	8, 785	1, 921
Plume Reheat Equipment	205	205	72	46	72
Sulfuric Acid Plant	4, 100	4, 100	1, 354	3, 690	-
Total Plant	19, 390	16, 230	4, 772	12, 521	1, 993
Working Capital	818	726	272	656	101
Total Investment	20, 208	16, 956	5, 044	13, 177	2, 094
Capital Requirements, $/kw	14. 43	12. 11	22. 93	-	9. 52

The capital requirement in terms of dollars per kilowatt of installed capacity is the lowest for the Simplified Lime Process, Case 3. This process is a relatively simple system since it does not have an absorbent regeneration section; nor does it require a sulfuric acid plant for SO_2 recovery.

B. OPERATING COSTS AND PROFITABILITY

The initial economic analyses of the cases evaluated in Phase III assumed a 90% plant factor (330 days operation per year). In Cases 1, 2 and 4 operations were considered to be continuous under these conditions. In Case 3, however, operations averaged 60% of capacity on the operating days, equivalent to a 54% plant factor. In all cases a plume reheat of $50^{o}F$ (a rise from 122^{o} to $172^{o}F$) was used.

The operating costs and profitability for these situations are summarized in Table 111. It is interesting to note that the net cost of Case 3 (220 Mw) of the Zinc Oxide Process is about the same as the cost of Case 3 of the Simplified Lime Process, if acid from the ZnO Process were saleable at about $23/ton.

The changes in operating costs and profitability due to adjustments in plant factor and plume reheat temperature are reflected in Table 112. The data indicate that operations in Cases 1 and 2 (1400 Mw) could break-even if sulfuric acid could be sold for $20-25/ton. Case 3 operations for both the Zinc Oxide and Simplified Lime Processes would operate at a substantial cost. Case 4, the New Smelter Facility, is not included in this tabulation since it would not be affected by the 70% plant factor of power plants.

TABLE 111

PROFITABILITY
PLANTS OPERATING AT 90% PLANT FACTOR - 330 DAYS PER YEAR
PLUME REHEAT FROM 122° TO 172°F

	Zinc Oxide Process											Lime
	Case 1			Case 2			Case 3*		Case 4			Case 3*
	Sulfuric Acid Price, $/ton											
	34	23.50	21.03	34	23.50	19.43	34	23.50	34	23.50	17.70	- 0 -
Sales, M tons H_2SO_4 **	380	380	380	380	380	380	44	44	324	324	324	- 0 -
Sales, M$	12,920	8,930	7,992	12,920	8,930	7,383	1,496	1,034	11,016	7,614	5,734	- 0 -
Operating Cost, M$												
Process	5,645	5,645	5,645	5,036	5,036	5,036	1,137	1,137	3,970	3,970	3,970	788
Plume Reheat	422	422	422	422	422	422	90	90	50	50	50	90
Sulfuric Acid	1,925	1,925	1,925	1,925	1,925	1,925	652	652	1,714	1,714	1,714	-
Total	7,992	7,992	7,992	7,383	7,383	7,383	1,879	1,879	5,734	5,734	5,734	878
Profit (loss) Before Tax, M$	4,928	938	- 0 -	5,537	1,547	- 0 -	(383)	(845)	5,282	1,880	- 0 -	(878)
Profit After Tax, M$	2,365	450	- 0 -	2,658	743	- 0 -	-	-	2,535	902	- 0 -	-
Return on Total Inv. A/T, %	11.7	2.2	- 0 -	15.6	4.4	- 0 -	-	-	19.2	6.8	- 0 -	-
Payout, years	4.5	7.8	9.5	3.8	6.7	9.5	-	-	3.4	5.8	9.5	-
Profit (loss) Before Tax												
$/ton of coal	1.07	0.20	- 0 -	1.21	0.34	- 0 -	(0.90)	(1.98)	-	-	-	(2.05)
mills/kwh	0.44	0.08	- 0 -	0.50	0.14	- 0 -	(0.37)	(0.81)	-	-	-	(0.84)
$/ton of H_2SO_4	12.97	2.47	- 0 -	14.57	4.07	- 0 -	(0.87)	(1.92)	16.30	5.80	- 0 -	-
Break-even Point, %	43	74	90	36	64	90	-	-	33	55	90	-

Note: Also see Tables 26 and 28 of Volume II.

[*] In Case 3, operations are at 330 days per year at 60% capacity.

[**] Assumes 95% SO_2 removal efficiency, 10% conversion of removed SO_2 to a discardable sulfate stream, and 96% conversion efficiency of remaining removed SO_2 to product sulfuric acid.

TABLE 112

PROFITABILITY

PLANTS OPERATING AT 70% PLANT FACTOR
PLUME REHEAT FROM 122° to 200°F

	Zinc Oxide Process								Lime
	Case 1			Case 2			Case 3		Case 3
	Sulfuric Acid Price, \$/ton								
	34	24.85	23.50	34	23.50	22.78	34	23.50	- 0 -
Sales, M tons H_2SO_4*	295	295	295	295	295	295	55.4	55.4	- 0 -
Sales, M\$	10,030	7,329	6,933	10,030	6,932	6,720	1,884	1,302	- 0 -
Operating Cost, M \$									
Process	5,082	5,082	5,082	4,473	4,473	4,473	1,225	1,225	892
Plume Reheat	502	502	502	502	502	502	106	106	106
Sulfuric Acid	1,745	1,745	1,745	1,745	1,745	1,745	618	618	-
Total	7,329	7,329	7,329	6,720	6,720	6,720	1,949	1,949	998
Profit (loss) Before Tax, M\$	2,701	- 0 -	(396)	3,310	212	- 0 -	(65)	(647)	(998)
Profit After Tax, M\$	1,296	- 0 -	-	1,589	102	- 0 -	-	-	-
Return on Total Inv., A/T, %	6.4	- 0 -	-	9.3	0.6	- 0 -	-	-	-
Payout, years	5.9	9.5	-	5.0	9.0	9.5	-	-	-
Profit (loss) Before Tax									
\$/ton of coal	0.76	- 0 -	(0.11)	0.93	0.06	- 0 -	(0.12)	(1.17)	(1.81)
mills/kwh	0.31	- 0 -	(0.05)	0.38	0.02	- 0 -	(0.05)	(0.48)	(0.74)
\$/ton of H_2SO_4	9.15	- 0 -	(0.17)	11.22	0.72	- 0 -	(1.17)	(11.68)	-
Break-even Point, %	43	70	78	37	66	70	73	-	-

Note: Also see Tables 25 and 27 of Volume II.

*Assumes 95% SO_2 removal efficiency, 10% conversion of removed SO_2 to a discardable sulfate stream, and 96% conversion efficiency of remaining removed SO_2 to product sulfuric acid.

PART FIVE

"FUTURE" WORK

As an extension of the effort described in Parts Two to Four relating to the removal of sulfur dioxide from flue gases by aqueous scrubbing methods, the following specific areas of investigation were considered to warrant additional effort (and this work was conducted under Phase IV of this study; see Volume II of this report for the results):

- Conceive new aqueous scrubbing processes (including the regeneration step) for the removal of SO_2 from the flue gases emanating from various industrial sources (of which, power plant and smelter effluents will be considered representative). Through appropriate laboratory investigations, develop these newly conceived processes by demonstrating their technical feasibility.
- Through appropriate laboratory investigations, develop improvements to previously-conceived aqueous scrubbing processes (or any portion thereof). An example here could be an investigation of how to minimize the effects of the disproportionation that occurs during the calcination of metallic sulfites (a regeneration step applicable to various aqueous processes).
- Through appropriate laboratory investigations, determine the degree to which inadvertent sorbent oxidation in aqueous scrubbers can be minimized by the utilization of various oxidation inhibitors and complexing agents (both with and without fly ash being present in the flue gas being tested).
    - Presuming that the degree of oxidation cannot be economically reduced by use of inhibitors or complexing agents, investigate the technical feasibility of separating the oxidation product from the scrubber effluent by chemical or ion-exchange means, followed by the thermal, chemical or electrochemical regeneration of the resultant material.
    - Complete the study that was begun under the initial contract that deals with the determination of the effects that pre-scrubbing has on the degree of oxidation in the main SO_2 scrubber.
- Through appropriate laboratory investigations, determine the degree of interference which inadvertent sorption of NO_x into SO_2 scrubbing solutions has on SO_2 removal efficiencies (both with and without fly ash being present in the flue gas being tested).

  - Assess the technical feasibility of achieving high NO_x removal efficiencies in conjunction with high SO_2 removal efficiencies.

- Support each of the above-mentioned laboratory investigations with preliminary process evaluations/designs/economic analyses to illustrate the economic feasibility of the concepts undergoing scrutiny in the laboratory (using either the Phase I or the Phase III approach of the initial contract, whichever is deemed appropriate).

PART SIX

BIBLIOGRAPHY

During the course of the Phase I effort an extensive list of references was acquired relating either directly or indirectly to some aspect of the aqueous scrubbing of sulfur dioxide from flue gases. The bibliography which follows is not intended to represent a complete coverage of the subject, but is believed to include the most important papers. Of the first 645 entries approximately 500 (those marked by an asterisk) have been acquired and catalogued by Aerojet, and many of these were utilized in the preparation of the present report.

The references have been categorized into six groups, which are considered in the following order: Articles, Patents (United States and Foreign), Reports, Government Publications, Books, and Theses and Dissertations. Within each group the listing is alphabetical by principal author. An index of all subsidiary authors is also provided for completeness.

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APPENDIX A

THEORETICAL CHEMICAL EQUILIBRIA CONSIDERATIONS

The following three equilibria govern the solubility of SO_2 in aqueous media:

the equilibrium between the gas and unionized dissolved SO_2

$$H_2SO_3 = SO_2\ (\text{gas}) + H_2O \qquad K_1 = \frac{P_{SO_2}}{(H_2SO_3)} \tag{A-1}$$

the first ionization of aqueous SO_2,

$$H_2SO_3 = H^+ + HSO_3^- \qquad K_2 = \frac{(H^+)(HSO_3^-)}{(H_2SO_3)} \tag{A-2}$$

the second ionization of aqueous SO_2,

$$HSO_3^- = H^+ + SO_3^= \qquad K_3 = \frac{(H^+)(SO_3^=)}{(HSO_3^-)} \tag{A-3}$$

Let s = the total concentration of SO_3 in solution, i.e.,

$$s = (H_2SO_3) + (HSO_3^-) + (SO_3^=) \tag{A-4}$$

Equations A-1 to A-3 can then be combined to yield Equation A-5 which relates the partial pressure of SO_2 over the solution, the total amount of SO_2 in solution, and the hydrogen ion concentration.

$$P_{SO_2} = \frac{K_1 (H^+)^2 s}{(H^+)^2 + K_2 (H^+) + K_2 K_3} \tag{A-5}$$

An examination of Equation A-5 indicates that the partial pressure of SO_2 in equilibrium with the solution can be reduced to any amount desired by reducing either the hydrogen ion concentration or the amount of SO_2 in the solution. Johnstone[224] gives the following values for K_1, K_2, and K_3 at 25°C:

$$K_1 = 0.795 \text{ atm/mole/1000 g } H_2O$$
$$K_2 = 0.013 \text{ mole/1000 g } H_2O$$
$$K_3 = 10^{-7} \text{ mole/1000 g } H_2O.$$

If the assumption is made that any scrubbing solution will have 1 mole/liter of SO_2 dissolved, then the partial pressure of SO_2 will be less than 150×10^{-6} atm in any solution in which the pH is higher than 5.6. These constants are temperature dependent and somewhat composition dependent.

The reader will note that many of the considerations which follow are also attributable to Johnstone. A charge-balance equation is necessary to relate the hydrogen ion concentration to that of other species present. Let M_i be the concentration of a charged ion species, i, and let Z_i be the charge (either a positive or a negative integer). All species other than H^+, HSO_3^-, OH^-, and $SO_3^=$ are considered. Then the net charge in the solution must be zero and Equation A-6 follows:

$$(H^+) + \sum_i Z_i M_i = (HSO_3^-) + 2(SO_3^=) + (OH^-). \tag{A-6}$$

The use of Equations A-2 and A-3 and the definition of s with Equation A-6 result in Equation A-7.

Substitution of Equations A-2, A-3, and A-6 in Equation A-4 and rearranging gives:

$$s = \frac{\left[(H^+) + \sum Z_i M_i - (OH^-)\right]\left[(H^+)^2 + K_2 (H^+) + K_2 K_3\right]}{K_2 (H^+) + 2 K_2 K_3} \tag{A-7}$$

Combining Equations A-5 and A-7 results in:

$$P_{SO_2} = \frac{K_1 (H^+)^2 \left[(H^+) + \sum Z_i M_i - (OH^-)\right]}{K_2 (H^+) + 2 K_2 K_3} \tag{A-8}$$

The hydrogen ion concentration can be eliminated from Equations A-7 and A-8 to provide an expression for s, the sulfur dioxide solubility, and P_{SO_2}, the partial pressure of SO_2, in terms of $\Sigma Z_i M_i$, the other constituents present.

As an example, consider the case in which ammonia is the only other species present in total concentration, C, and in acid solution of pH 4-7. Then $(NH_4^+) = \Sigma Z_i M_i = C$ and

$$(OH^-) << (H^+) << 1,$$

$$(H^+)^2 << K_2 (H^+)$$

Equation A-7 thus becomes: $(H^+) = \frac{(2\,S - C)}{(C - S)} K_3$

and Equation A-8 becomes: $P_{SO_2} = \frac{K_1 K_3}{K_2} \frac{(2\,S - C)^2}{(C - S)}$

$\frac{K_1 K_3}{K_2}$ can be combined in one constant, M, which is a function of temperature and depends slightly on concentration. Johnstone[224] gives a measured value for M in ammonia of 20×10^{-6} atm/mole/liter H_2O at 25°C which agrees fairly well with the calculated $K_1 K_3 / K_2$ of 6.1×10^{-6} atm/mole/liter H_2O assuming ideal solution.

Johnstone has also developed a series of equations to represent the results of the measurement of SO_2 pressure over concentrated alkaline solutions.[676]

$$P_{SO_2} = F(T) \frac{(2\,S - C)^2}{C - S}$$

where: P_{SO_2} = SO_2 pressure in mm

S = Total SO_2 in solution, moles/100 moles H_2O

C = Total moles of base in solution, moles/100 moles H_2O

F (T) = 0.0343 for ammonia solutions at 50°C

F (T) = 0.0233 for sodium hydroxide solutions at 50°C.

These numbers were used in deriving the values for the ammonia and sodium hydroxide scrubber systems shown in Table 2 of the text.

The question arises as to whether carbon dioxide will displace SO_2 from an aqueous solution and decrease the capacity of the solution for absorbing SO_2. The equilibrium involved in an aqueous solution in which all the constituents are soluble is:

$$CO_2 + HSO_3^- = SO_2 + HCO_3^-$$

Using the thermodynamic functions from Latimer[671] (see Table A-1), the free energy change of this reaction is found to be +8.2 kcal at 25°C and the entropy change is +5.04 entropy units. Since the entropy change is positive, the reaction is driven to the right by raising the temperature. As a first approximation for the temperature correction in raising the system to 50°C, the heat capacities of the substances represented on both sides of the equation can be assumed to be equal. Since $d\Delta F^o/dT = -\Delta S^o$, ΔF^o at $50^o = \Delta F^o$ at $25^o - 25\,\Delta S^o = 8.0 = -RT \ln K$.

The equilibrium constant for the reaction at 50°C is estimated to be 4×10^{-6}. Then:

$$\frac{(HCO_3^-)}{(HSO_3^-)} = K\, P_{CO_2}/P_{SO_2}$$

At the bottom of the scrubber where $P_{CO_2} = 112$ mm and $P_{SO_2} = 2.28$ mm, the bicarbonate to bisulfate ratio is 2×10^{-4}. This means that virtually none of the aqueous base at the bottom of the scrubber is in the form of bicarbonate and is therefore used in absorbing SO_2.

The situation for slurries of basic oxides is somewhat different. For both calcium and magnesium oxides, the 14.7% partial pressure of carbon dioxide in flue gases is sufficient to convert the oxide to the carbonate. Hence, the net reaction to be considered is $MCO_3 + SO_2 = MSO_3 + CO_2$, where M represents either calcium or magnesium.

TABLE A-1

THERMODYNAMIC DATA ON SOME COMPOUNDS OF INTEREST

Formula	State	H^o kcal/mole	F^o kcal/mole	S^o cal/deg K
Ca^{++}	aq	-129.77	-132.18	-13.2
CaO	C	-151.9	-144.4	9.5
$Ca(OH)_2$	C	-235.8	-214.33	18.2
$CaSO_3$	C	-	-	24.2
$CaCO_3$	C	-288.45	-269.78	22.2
CO_2	g	-94.0518	-94.2598	51.061
CO_2	aq	-98.69	-92.31	29.0
H_2CO_3	aq	-167.0	-149.00	45.7
HCO_3^-	aq	-165.18	-140.31	22.7
$CO_3^=$	aq	-161.63	-126.22	-12.7
H^+	aq	0	0	0
OH^-	aq	-54.957	-37.595	-2.52
H_2O	aq	-68.317	-56.690	16.716
H_2O	g	-57.798	-54.635	45.106
Mg^{++}	aq	-110.41	-108.99	-28.2
MgO	C	-143.84	-136.13	6.4
$Mg(OH)_2$	C	-221.00	-199.27	15.09
$MgSO_3$	C	-241.0	-221.2	22.5
$MgCO_3$	C	-266.	-246.	15.7
SO_2	g	-70.76	-71.79	59.4
SO_2	aq	-80.86		
HSO_3^-	aq	-151.9	-126.0	26.
H_2SO_3	aq	-145.5	-128.59	56.
$SO_3^=$	aq	-151.9	-116.1	-7.

The free energy of formation of calcium sulfite is estimated to be -255.25 kcal/mole. This value is derived from Latimer's free energies of the separate ions and from the solubility product of calcium sulfite. The following table can then be derived:

Reaction	F^o (kcal/mole)	K	P_{SO_2} in 14.7% (mm) CO_2
a. $CaCO_3 + SO_2 = CaSO_3 + CO_2$	-7.9	6.6×10^5	1.7×10^{-4}
b. $MgCO_3 + SO_2 = MgSO_3 + CO_2$	+2.33	0.02	5600
c. $MgCO_3 + H_2O + 2\,SO_2 =$ $Mg^{++} + 2\,HSO_3^- + CO_2$	-9	4×10^6	5×10^{-3}
d. $CaCO_3 + H_2O + 2\,SO_2 =$ $Ca^{++} + 2HSO_3^- + CO_2$	-8.39	1.4×10^6	9×10^{-3}

These values indicate that if the carbon dioxide pressure is higher than 1.7×10^{-4} mm, Reaction (d), with calcium carbonate, will occur. With magnesium carbonate, Reaction (b) will not occur unless the SO_2 pressure is higher than 5600 mm, but Reaction (c) will occur if the carbon dioxide pressure is higher than 5×10^{-3} mm.

At the top of the scrubber, where the SO_2 pressure is 0.1 mm (0.015%), these numbers indicate that SO_2 will be absorbed by calcium carbonate with the formation, in solution, of calcium bisulfite. A small change in the values of the equilibrium constants would suggest that calcium sulfite would be precipitated.

Magnesium carbonate would be expected to absorb SO_2 with the liberation of carbon dioxide and there is small likelihood of the precipitation of magnesium sulfite. These results are consistent with the fact that calcium sulfite is much less soluble than magnesium sulfite. A temperature correction has not been applied. The uncertainty in the data is much larger than the factor of about 0.2 kcal/mole correction to the free energy which is needed for the temperature correction.

The conclusions to be drawn from these data are that:

- Calcium or magnesium oxide slurries in amounts in excess of the amount of SO_2 present will absorb carbon dioxide and be converted to the carbonates.

- Both calcium and magnesium carbonate are basic enough to absorb SO_2 at the 0.015% level with calcium having the larger driving potential.

- There is a moderate possibility of precipitating calcium sulfite, even in fairly dilute solutions.

- There is nothing in the available thermodynamic data to indicate that calcium or magnesium oxide slurries are incapable of reducing SO_2 partial pressures to 0.015%.

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APPENDIX B

CONVERSION OF GASEOUS SULFUR DIOXIDE TO MARKETABLE PRODUCTS: COST ESTIMATES

GENERAL

Many of the processes discussed in this report yield sulfur dioxide as a by-product. For each of these systems, both the capital and operating costs required to liquefy the sulfur dioxide were included in the total costs.

The potential quantities of sulfur dioxide produced by recovery from flue gas are so large that it is unlikely that the market for liquid SO_2 could absorb this production. Since approximately 80% of the natural sulfur mined annually is converted to sulfuric acid, it is logical to assume that the optimum usage for sulfur dioxide recovered from flue gas should be in the production of sulfuric acid. The following three approaches are available for accomplishing this goal:

- Liquefy the sulfur dioxide for shipment to sulfuric acid producers.
- Produce sulfuric acid from the recovered gaseous sulfur dioxide at the power plant site.
- Reduce the gaseous sulfur dioxide to elemental sulfur, which in turn can be converted to sulfuric acid as warranted.

The selection of the specific route would depend on the sulfuric acid market, on the existing sulfuric acid producers in the locality of each power plant, and on relative shipping costs.

Order-of-magnitude capital and operating cost estimates have been prepared for each of the three approaches. These are presented below.

LIQUEFACTION OF SULFUR DIOXIDE

The theoretical quantity of sulfur dioxide produced in most of the processes which yield SO_2 as a by-product is 34,610 tons per year. This is based on the standards of the 120-megawatt power plant used in Phase I of this study.

Capital Costs

As mentioned in the general discussion above, these costs have been included in the total capital cost of each process, where applicable. The purchased equipment cost, taken from the Bureau of Mines study,[621] is $102,000. This provides a fixed capital cost of $483,500 and a total investment including working capital of $531,400. The capital requirements are: $4.43 per kw capacity, and $15.25 per ton SO_2 produced. All of these values are deductible from the specific process capital costs to obtain the net process costs.

Operating Costs

The operating costs have been summarized in Table B-1. Purchased raw materials are not required. Direct labor has been estimated at one man per shift. The supervision requirement has not been increased, since it would be provided from the SO_2 recovery system operation. Utilities requirements are 138,000 kwh electricity and 623,000 M gal circulating cooling water.

SULFURIC ACID PRODUCTION

The sulfur dioxide recovered would yield approximately 50,000 tons of 100% sulfuric acid per year. The most economical production cost would be in a system where the gaseous SO_2 could be converted directly to sulfuric acid at the power plant site.

Capital Costs

Capital investment required for a contact process sulfuric acid plant varies from $12,500 per ton for a 100-ton per day plant to $10,000 per ton for a 240-ton per day plant.[653] A 150-ton per day acid plant at $12,500 per ton would cost $1,875,000. Adding working capital, the capital requirement is $2,062,500, or $17.20 per kw capacity. This corresponds to $59.60 per ton SO_2 converted and $41.25 per ton H_2SO_4 produced.

Operating Costs

The reference cited[653] lists the following requirements per ton of 100% sulfuric acid produced:

Labor	-	0.64 man hour
Electricity	-	5 kwh
Water	-	4,000 gal
Steam	-	200 lb
Air	-	250,000 cu. ft.

The direct labor requirement is 32,000 man hours, or 16 men (4 per shift). One foreman per shift has been charged to the system.

TABLE B-1

LIQUEFACTION OF SO_2*: OPERATING COST ESTIMATE SUMMARY

Fixed Capital Cost: $483,500

	ITEM	TOTAL $	%
1.	Raw Materials & Chemicals	-	-
2.	Direct Labor	24,000	13.90
3.	Supervision	--	-
4.	Maintenance, 5% of Fixed Capital	24,200	13.96
5.	Supplies, 15% of Maintenance	3,600	2.08
6.	Utilities	31,800	18.41
7.	Other	-	-
8.	TOTAL DIRECT COST	83,600	48.35
9.	Payroll Burden, 20% of 2 & 3	500	0.29
10.	Plant Overhead, 50% of 2, 3, 4 & 5	25,900	15.00
11.	Pack & Ship	-	-
12.	Waste Disposal	-	-
13.	Other	-	-
14.	TOTAL INDIRECT COST	26,400	15.29
15.	Depreciation, 10 % Fixed Capital/Yr	48,400	27.96
16.	Taxes, 2% of Fixed Capital	9,700	5.62
17.	Insurance, 1% of Fixed Capital	4,800	2.78
18.	Other	-	-
19.	TOTAL FIXED COST	62,900	36.36
20.	TOTAL OPERATING COST	172,900	100.00

21.	COST:	$/Ton of Coal	0.36
22.		Mill/kwh	0.18
		$/Ton SO_2	5.00

$/Long Ton S Equivalent: 11.20

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*34,610 tons per year

The utility requirements are:

Power - 250,000 kwh per year
Water - 200,000 M gal per year
Steam - 10,000 M lb per year

Table B-2 summarizes the operating costs. The operating cost of \$12.97 per ton of 100% sulfuric acid may have some significance since the cost of purchased sulfur to produce one ton of 100% sulfuric acid in a conventional plant is \$11.40 (0.3 long ton S at \$38/long ton). Addition of this raw material cost would increase the operating cost to \$24.37 in a conventional sulfuric acid plant. The manufacturing cost in large sulfuric acid plants is undoubtedly less than \$24.37 per ton 100% H_2SO_4. This cost comparison, however, illustrates the possible cost reductions achievable by eliminating the raw material cost in sulfuric acid production via the contact process.

A recent announcement[73] indicates that sulfuric acid could be produced from gypsum in a large plant for \$16 per ton. Investment for a 1500-ton-per-day sulfuric acid plant (and a roughly equivalent amount of cement by-product) would be about \$30 million.

REDUCTION OF SULFUR DIOXIDE TO SULFUR

Reference[635] is made in the literature to the Guggenheim process, a method in which the SO_2 is reduced to sulfur. The SO_2 is mixed with 25 percent air, preheated to 400°C, and passed through a coke bed which is maintained incandescent (800°C) by the reaction between coke and air. The gases pass through the reduction chamber at such a rate that a substantial amount of SO_2 remains. The exit gases, which contain sulfur, carbonyl sulfide (COS), carbon disulfide (CS_2), and SO_2 are passed to a second chamber containing a pumice catalyst; the carbon-containing compounds react with SO_2 to form sulfur and CO. the sulfur is then condensed and the exit gases are returned to the absorption system.

Capital Costs

No recent cost data were found in the literature. The reference mentioned above states that the capital cost amounts to \$15 per ton of sulfur per year.

TABLE B-2

PRODUCTION OF SULFURIC ACID FROM GASEOUS SO_2*: OPERATING COST ESTIMATE SUMMARY

Fixed Capital Cost: $1,875,000

	ITEM	TOTAL $	%
1.	Raw Materials & Chemicals	-	-
2.	Direct Labor	96,000	14.81
3.	Supervision	31,200	4.81
4.	Maintenance, 5% of Fixed Capital	93,800	14.47
5.	Supplies, 15% of Maintenance	14,100	2.17
6.	Utilities	26,500	4.08
7.	Other	-	-
8.	TOTAL DIRECT COST	261,600	40.34
9.	Payroll Burden, 20% of 2 & 3	25,400	3.92
10.	Plant Overhead, 50% of 2, 3, 4 & 5	117,600	18.14
11.	Pack & Ship	-	-
12.	Waste Disposal	-	-
13.	Other	-	-
14.	TOTAL INDIRECT COST	143,000	22.06
15.	Depreciation, 10 % Fixed Capital/Yr	187,500	28.92
16.	Taxes, 2% of Fixed Capital	37,500	5.78
17.	Insurance, 1% of Fixed Capital	18,800	2.90
18.	Other	-	-
19.	TOTAL FIXED COST	243,800	37.60
20.	TOTAL OPERATING COST	648,400	100.00

21.	COST:	$/Ton of Coal	1.36
22.		Mill/kwh	0.68
		$/Ton H_2SO_4	12.97

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*50,000 short tons SO_2 per year

The Marshall and Stevens Index was used to convert this 1937 cost to present day costs; the C. E. Index was not used since it was not developed until 1947. Since the slope of the M & S Index for the post 1947 period is practically the same as the C. E. Index, its use is considered to lead to costs which are comparable to other factored costs in this study. The M & S Index indicates a three-fold increase in capital costs between 1937 and 1967. On this basis, it was assumed that the capital cost for the SO_2 reduction system would be $45 per ton of sulfur per year, or approximately $780,000 in fixed capital cost. Adding 10% for working capital, the unit costs are $7.15 per kw capacity, a value equivalent to $24.80 per ton SO_2 converted or $55.50 per long ton S produced.

Operating Costs

Table B-3 summarizes the operating costs. The raw material cost is for coke at the rate of 0.75 ton of coke per ton sulfur. On this basis, approximately 13,000 tons of coke per year are required.

A direct labor requirement of one man per shift is considered adequate. Supervision can be provided from the SO_2 absorption plant operation.

The utility requirements are as follows:

Power (for preheating SO_2 gas):	2×10^{10} BTU per year
Circulating Water (for cooling the sulfur and carbon monoxide and condensation and cooling of sulfur to 300°C):	36,300 M gal per year

TABLE B-3

REDUCTION OF GASEOUS SO_2 TO ELEMENTAL SULFUR*: OPERATING COST ESTIMATE SUMMARY

Fixed Capital Cost: $778,500

	ITEM	TOTAL $	%
1.	Raw Materials & Chemicals	247,000	51.26
2.	Direct Labor	24,000	4.98
3.	Supervision	-	-
4.	Maintenance, 5% of Fixed Capital	38,900	8.07
5.	Supplies, 15% of Maintenance	5,800	1.20
6.	Utilities	30,000	6.23
7.	Other	-	-
8.	TOTAL DIRECT COST	345,700	71.74
9.	Payroll Burden, 20% of 2 & 3	500	0.10
10.	Plant Overhead, 50% of 2, 3, 4 & 5	34,400	7.14
11.	Pack & Ship	-	-
12.	Waste Disposal	-	-
13.	Other	-	-
14.	TOTAL INDIRECT COST	34,900	7.24
15.	Depreciation, 10 % Fixed Capital/Yr	77,900	16.16
16.	Taxes, 2% of Fixed Capital	15,600	3.24
17.	Insurance, 1% of Fixed Capital	7,800	1.62
18.	Other	-	-
19.	TOTAL FIXED COST	101,300	21.02
20.	TOTAL OPERATING COST	481,900	100.00

21.	COST:	$/Ton of Coal	1.02
22.		Mill/kwh	0.51
		$/L ton S	31.19

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*15,450 L. tons sulfur per year

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APPENDIX C-1

Acknowledgments

The contributions of the following equipment companies are acknowledged.

Allis Chalmers
Bird Machine Company
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Buffalo Forge Company
The Ceilcote Company
Chemineer, Inc.
Chicago Bridge and Iron Company
Copolymer Corporation
De Laval Separator Company
Dorr-Oliver, Inc.
The Eimco Corporation
FMC Corporation - Hydrodynamics Division
Goulds Pumps, Inc.
Ingersoll-Rand Company
Joy Manufacturing Company
Parker Brothers, Inc.
Sprout Waldron and Company, Inc.
Struthers-Wells Corporation
U. S. Stoneware, Inc.
UOP Air Correction Division

APPENDIX C-2

ZINC OXIDE PROCESS

Case 1 & 2

Equipment List

Item C1 - Flue Gas Blower (2 required)

Capacity:	1,675,000 ACFM @ 500 RPM
Static Pressure:	5 in. S.W.G.
Motor HP:	2250
Brake HP:	2140
Fan Diameter:	15 ft
Diffuser:	40 ft long x 21 ft exit diameter
Weight:	70,000 lb
Price:	$128,000

Item C2 - Dryer Gas Blower (1 required)

Capacity:	311,650 ACFM @ 558 RPM
Static Pressure:	5 in. S.W.G.
Motor HP:	350
Brake HP:	330
Wheel Diameter:	7 ft 5 in.
Price:	$39,200

Item C3 - SO_2 Recycle Compressor (1 required)

Capacity:	1890 ACFM @ 3160 RPM
Intake Pressure:	14.7 psia
Discharge Pressure:	22.7 psia
Intake Temperature:	120°F
Discharge Temperature:	203°F
Motor HP:	100
Brake HP:	83
Price:	$6863

Item E1 - SO_2-H_2O Condenser (1 required)

Type:	Direct contact packed column
Size:	12 ft dia x 20 ft high steel column epoxy resin coated
Packing:	904 cu ft 3 in. stoneware, Intalox saddles
ΔP:	2.4 in. S.W.G. across packing
Price:	$17,000

Item E2 - Heat Exchanger (1 required)

Duty: 81,000,000 Btu/hr
Area: 7650 sq ft
Size: 34 in. I.D. steel shell
Tubes: 3/4 in. O.D. x 20 ft long, type 316 SS
Tube Plates: C.S. clad with type 316 SS
Max. Oper. Pressure: 100 psig, both tube side and shell side
Price: $46,170

Item M1 - Ash Filter (2 required)

Type: Vacuum Drum Filter, 12 ft dia. x 14 ft long, 532 sq ft rubber-covered; complete with filtrate receiver, moisture trap, filtrate pump and vacuum pump.
Capacity: 163 tons/day dry cake
Total Motor HP: 81.5
Price: $55,220

Item M2 - Zinc Sulfite Centrifuge (5 required)

Type: 36 in. x 96 in. screen bowl centrifuge
Motor HP: 250
Capacity: 26 ton/hr dry solids
Price: $65,000

Item M3 - Zinc Sulfite Dryer (1 required)

Type: Rotary dryer, concurrent flow, indirect heating
Capacity: 4300 lb/min zinc sulfite with 20% free water dried to a product containing not more than 2% free water.
Size: 11 ft diameter x 100 ft long
Motor HP: 250
Price: $157,500

Item M4 - Hammer Mill (3 required)

Type: 18 in., direct-coupled, 1800 RPM
Motor HP: 50
Capacity: 43 ton/hr, -100 mesh
Price: $3110

Item M5 - Flash Calciner (1 required)

Type:	Vertical furnace with stainless steel radiant tubes for continuous operation of 1400°F wall temperature.
Heat Duty:	176 million Btu/hr
Capacity:	130 tons per hour of zinc sulfite - 2-1/2 H_2O with 2% free water, heating it to 600°F minimum thereby flashing off water and sulfur dioxide.
Feed Temperature:	200°F
Price:	$440,000

Item M6 - Zinc Sulfite Conveyor (2 required)

Type:	Screw conveyor, enclosed
Size:	20 in. dia x 100 ft long
Capacity:	2650 lb/min wet cake
Material of Construction:	Coated steel
Motor HP:	25
Price:	$9300

Item M7 - Zinc Sulfite Conveyor (1 each required)

a.	Type:	Screw conveyor, enclosed
	Size:	20 in. dia x 120 ft long
	Capacity:	4300 lb/min dry material
	Motor HP:	25
	Price:	$11,000
b.	Type:	16 x 8 bucket, 60 ft vertical
	Capacity:	4300 lb/min dry material
	Motor HP:	20
	Price:	$5300

Item M8 - Zinc Oxide Conveyor (1 each required)

a.	Type:	Screw conveyor, enclosed
	Size:	20 in. dia x 45 ft long
	Capacity:	1840 lb/min
	Motor HP:	5
	Price:	$4700
b.	Type:	16 x 8 bucket, 30 ft vertical
	Capacity:	1840 lb/min
	Motor PH:	10
	Price:	$3800

Item M9 - Lime Hopper/Feeder (1 required)

Surge Capacity: 50 cu ft
Feed Capacity: 106 lb/min
Motor HP: 1
Price: $6,000

Item M10 - Soda Ash Hopper/Feeder (1 required)

Surge Capacity: 50 cu ft
Feed Capacity: 10 lb/min
Motor HP: 1
Price: $6,000

Item M11 - Zinc Oxide Hopper/Feeder (1 required)

Surge Capacity: 50 cu ft
Feed Capacity: 5 lb/min
Motor HP: 1
Price: $6,000

Item M12 - Zinc Sulfite Hopper/Feeder (1 required)

Surge Capacity: 500 cu ft
Feed Capacity: 4300 lb/min
Motor HP: 10
Price: $13,000

Item M13 - Waste Conveyor (1 required)

Type: 12 in. inclined belt, 150 ft long
Capacity: 540 lb/min
Motor HP: 15
Price: $6,400

Item M14 - Furnace (1 required)

Type: Gas or oil-fired standard combustion chamber
Heat Duty: 53 million Btu/hr
Price: $50,000

Item P1 - Rich Solution Pump (2 required)

Type: Centrifugal
Capacity: 5000 gpm
Discharge Pressure: 24 ft
Size: 14 x 14 x 20
Motor HP: 50
Brake HP: 43.1
Material of Construction: 316 SS
Price: $6,050

Item P2 - Clarifier Slurry Pump (1 required)

Type: Centrifugal
Capacity: 870 gpm
Discharge Pressure: 30 ft
Size: 6 x 4 x 13
Motor HP: 10
Material of Construction: 316 SS
Price: $1,727

Item P3 - Zinc Sulfite Slurry Pump (1 required)

Type: Centrifugal
Capacity: 2060 gpm
Discharge Pressure: 65 ft
Size: 10 x 8 x 11
Motor HP: 50
Brake HP: 44.1
Material of Construction: Cast Iron
Price: $1,076

Item P4 - Lean Solution Pump (2 required)

Type: Centrifugal
Capacity: 5500 gpm
Discharge Pressure: 65 ft
Size: 14 x 14 x 20
Motor HP: 150
Brake HP: 124
Material of Construction: Cast Iron
Price: $3,828

Item P5 - Water Pump (2 required)

Type:	Centrifugal
Capacity:	2000 gpm
Discharge Pressure:	60 ft
Size:	10 x 8 x 11
Motor HP:	40
Brake HP:	36.2
Material of Construction:	316 SS
Price:	$2,480

Item P6 - Gasifier Liquid Pump (1 required)

Type:	Centrifugal
Capacity:	1000 gpm
Discharge Pressure:	30 ft
Size:	6 x 4 x 13
Motor HP:	15
Material of Construction:	316 SS
Price:	$1,787

Item P7 - Thickener Slurry Pump (1 required)

Type:	Centrifugal
Capacity:	300 gpm
Discharge Pressure:	25 ft
Size:	4 x 3 x 8
Motor HP:	5
Brake HP:	2.81
Material of Construction:	316 SS
Price:	$838

Item P8 - Liming Tank Slurry Pump (1 required)

Type:	Centrifugal
Capacity:	885 gpm
Discharge Pressure:	30 ft
Size:	6 x 4 x 13
Motor HP:	10
Material of Construction:	316 SS
Price:	$1,727

Item V1 - Flue Gas Cyclone (1 system required)[*]

Capacity:	4,185,000 ACFM, 300°F, 732 mm (wet) Inlet Fly Ash: 435 lb/min Outlet Fly Ash: 43.5 lb/min
Pressure:	Inlet: -15 in. of water Outlet: -19 in. of water
Construction:	Welded and flanged carbon steel
Price:	$769,000

Item V2 - Dryer Cyclone (1 system required)

Capacity:	291,500 ACFM, 250°F, 760 mm gas from dryer. Average mole weight: 35.6 (wet). Contains 0.71 lb $ZnSO_3 \cdot 2\text{-}1/2\ H_2O$ per 1000 SCF.
Pressure:	Inlet: -5 in. of water Outlet: -10 in. of water
Construction:	Welded and flanged carbon steel
Price:	$77,000

Item V3 - Wet SO_2 Cyclone (1 system required)

Capacity:	61,000 ACFM, 600°F, 760 mm SO_2 containing 0.7 lb H_2O/lb SO_2. Contains 0.66 lb ZnO dust per 1000 SCF.
Pressure:	Inlet: +1 in. of water Outlet: -4 in. of water
Construction:	Welded and flanged carbon steel clad with type 316 SS as required.
Price:	$46,800

Item V4 - Flue Gas Scrubber (quantity - see below)

Capacity:	Absorb 95 mole-% of the SO_2 from 2.75 MMSCFM of inlet flue gas containing 0.30% SO_2
Pressure Drop:	1 in. of water with inlet pressure of 724.5 mm Hg.
Liquid Rate:	10,870 gpm of sodium sulfite·bisulfite solution at 120°F

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[*] This item or equivalent is assumed to be furnished in existing plant - Case 2.

Item V4 (continued)

Type and Size:	Counter-current packed tower(s) containing a cross-sectional area of 10,936 sq ft packed with 3-in. polypropylene Intalox saddles to a depth of 8 ft. Total packing volume of approximately 87,600 cu ft. Over-all height approximately 40 ft allowing for 200,000 gal reservoir, gas inlet, packing support, packing, packing hold-down, liquid distributor, mist eliminator and gas outlet.
Materials of Construction:	Fiberglass reinforced plastic and/or steel-lined with protective coating.
Price:	$800,000

Although the quantity of scrubbers is not specified, it is assumed that at least 5 scrubbers in parallel would be used due to the large total cross-sectional area required.

Item V5 - Clarifier (1 required)

Capacity:	Settle and concentrate all of the ash and calcium sulfite precipitate contained 11,100 gpm of feed solution into an outlet slurry. The overflow shall contain less than 2 ppm solids.
Volume:	1,100,000 gal
Description:	140 ft dia x 10 ft SWD resin-coated steel tank, including thickener mechanism, walkway and handrails.
Motor HP:	10
Price:	$99,100

Item V6 - Waste Thickener (1 required)

Capacity:	Settle and concentrate all of the ash and calcium sulfate precipitate contained in 1020 gpm feed solution into an outlet slurry. The overflow shall contain less than 50 ppm of suspended solids.
Volume:	140,000 gal
Description:	50 ft dia x 10 ft SWD resin-coated steel tank, including thickener mechanism, walkway and handrails.
Motor HP:	2
Price:	$25,100

Item V7 - Zinc Oxide Tank (1 required)

Volume: 30,000 gal
Description: 23 ft dia x 10 ft SWD resin-coated steel tank with agitator
Agitator: 60 HP
Price: $16,500

Item V8 - Crystallizer Tank (1 required)

Volume: 150,000 gal
Description: 50 ft dia x 10 ft SWD resin-coated steel tank with agitator
Agitator: 250 HP
Price: $48,800

Item V9 - Gasifier Tank (1 required)

Volume: 30,000 gal
Description: 23 ft dia x 10 ft SWD resin-coated covered steel tank
Price: $8,300

Item V10 - Liming Tank (1 required)

Volume: 50,000 gal
Description: 33 ft dia x 8 ft SWD resin-coated steel tank with two compartments. Agitators in both compartments
Agitator: 40 HP
Price: $19,700

Item V11 - Lean Solution Surge Tank (1 required)

Volume: 210,000 gal
Description: 60 ft dia x 10 ft SWD resin-coated steel tank
Price: $24,300

Item V12 - Zinc Sulfite Filter Cake Hopper (1 required)

Volume: 2900 cu ft
Description: Rectangular resin-lined steel vessel with Vee bottom to a screw conveyor
Conveyor: 25 HP
Price: $35,000

Item V13 - Dry Zinc Sulfite Hopper (1 required)

Volume:	2700 cu ft
Description:	Rectangular steel vessel with Vee bottom to a screw conveyor
Conveyor:	25 HP
Price:	$30,000

Item V14 - Zinc Sulfite Thickener (1 required)

Capacity:	Settle and concentrate all of the zinc sulfite precipitate contained in 9100 gpm of feed solution into an outlet slurry. The overflow shall contain less than 2 ppm solids.
Volume:	1,100,000 gal
Description:	140 ft dia x 10 ft SWD resin-coated steel tank, including thickener mechanism, walkway and handrails.
Motor HP:	10
Price:	$99,100

APPENDIX C-3

ZINC OXIDE PROCESS

Case 3

Equipment List

Item C1 - Flue Gas Blower (1 required)

Capacity: 671,000 ACFM @ 500 RPM
Static Pressure: 5 in. S.W.G.
Motor HP: 800
Brake HP: 780
Fan Diameter: 11 ft
Diffuser: 26.6 ft long x 15 ft exit diameter
Weight: 50,000 lb
Price: $72,000

Item C2 - Dryer Gas Blower (1 required)

Capacity: 59,050 ACFM @ 1110 RPM
Static Pressure: 10 in. S.W.G.
Motor HP: 125
Brake HP: 115
Wheel Diameter: 4 ft 6-1/4 in.
Price: $8,800

Item C3 - SO_2 Recycle Compressor (1 required)

Capacity: 358 ACFM @ 3140 RPM
Intake Pressure: 14.7 psia
Discharge Pressure: 22.7 psia
Intake Temperature: 120°F
Discharge Temperature: 205°F
Motor HP: 20
Brake HP: 17.3
Price: $3,880

Item E1 - SO_2-H_2O Condenser (1 required)

Type: Direct contact packed column
Size: 5 ft- 3 in. dia. x 20 ft high steel column epoxy resin coated
Packing: 172 cu ft 3 in. stoneware, Intalox saddles
ΔP: 2.4 in. S.W.G. across packing
Price: $6,300

Item E2 - Heat Exchanger (1 required)

Duty:	15, 300, 000 Btu/hr
Area:	1530 sq ft
Size:	22 in. dia steel shell
Tubes:	3/4 in. O. D. x 20 ft long, type 316 SS
Tube Plates:	C.S. clad with type 316 SS
Max. Oper. Pressure:	100 psig, both tube side and shell side
Price:	$10, 680

Item M1 - Ash Filter (1 required)

Type:	Vacuum Drum Filter, 8 ft dia x 8 ft long, 200 sq ft, rubber-covered. Complete with filtrate receiver, moisture trap, filtrate pump, and vacuum pump.
Capacity:	61.6 tons/day dry cake
Total Motor HP:	36
Price:	$28, 620

Item M2 - Zinc Sulfite Centrifuge (2 required)

Type:	24 in. x 60 in. screen bowl centrifugal
Motor HP:	75
Capacity:	13 ton/hr dry solids
Price:	$38, 000

Item M3 - Zinc Sulfite Dryer (1 required)

Type:	Rotary dryer, concurrent flow, indirect heating.
Capacity:	815 lb/min zinc sulfite with 20% free water dried to a product containing not more than 2% free water.
Motor HP:	50
Price:	$60, 000

Item M4 - Hammer Mill (3 required)

Type:	14 in., direct-coupled, 1800 RPM
Motor HP:	50
Capacity:	8 ton/hr, -100 mesh
Price:	$2,520

Item M5 - Flash Calciner (1 required)

Type:	Vertical furnace with stainless steel radiant tubes for continuous operation at 1400°F wall temperature.
Heat Duty:	34 million Btu/hr
Capacity:	24.4 tons per hour of zinc sulfite·2-1/2 H_2O with 20% free water, heating it to 600°F minimum thereby flashing off water and sulfur dioxide.
Feed Temperature:	200°F
Price:	$140,000

Item M6 - Zinc Sulfite Conveyor (1 required)

Type:	Screw conveyor, enclosed
Size:	16 in. dia x 100 ft long
Capacity:	1000 lb/min wet cake
Materials of Construction:	Coated steel
Motor HP:	15
Price:	$7,500

Item M7 - Zinc Sulfite Conveyor (1 each required)

a. Type:	Screw conveyor, enclosed
Size:	12 in. dia x 120 ft long
Capacity:	815 lb/min dry material
Motor HP:	5
Price:	$5,100

b. Type:	8 x 5 bucket, 60 ft vertical
Capacity:	815 lb/min dry material
Motor HP:	5
Price:	$3,400

Item M8 - Zinc Oxide Conveyor (1 each required)

a. Type: Screw conveyor, enclosed
Size: 14 in. x 45 ft long
Capacity: 348 lb/min
Motor HP: 1
Price: $2, 700

b. Type: 6 x 4 bucket, 30 ft vertical
Capacity: 348 lb/min
Motor HP: 1.5
Price: $1, 100

Item M9 - Lime Hopper/Feeder (1 required)

Surge Capacity: 10 cu ft
Feed Capacity: 21 lb/min
Motor HP: 0.5
Price: $2, 500

Item M10 - Soda Ash Hopper/Feeder (1 required)

Surge Capacity: 10 cu ft
Feed Capacity: 2 lb/min
Motor HP: 0.5
Price: $2, 500

Item M11 - Zinc Oxide Hopper/Feeder (1 required)

Surge Capacity: 10 cu ft
Feed Capacity: 1 lb/min
Motor HP: 0.5
Price: $2, 500

Item M12 - Zinc Sulfite Hopper/Feeder (1 required)

Surge Capacity: 100 cu ft
Feed Capacity: 815 lb/min
Motor HP: 3
Price: $3, 500

Item M13 - Waste Conveyor (1 required)

Type:	12 in. inclined belt 150 ft long
Capacity:	100 lb/min
Motor HP:	3
Price:	$5,000

Item M14 - Furnace (1 required)

Type:	Gas or oil-fired standard combustion chamber
Heat Duty:	10 million Btu/hr
Price:	$20,000

Item P1 - Rich Solution Pump (1 required)

Type:	Centrifugal
Capacity:	1920 gpm
Discharge Pressure:	24 ft
Size	10 x 8 x 11
Motor HP:	25
Brake HP:	19
Material of Construction:	316 SS
Price:	$2,295

Item P2 - Clarifier Slurry Pump (1 required)

Type:	Centrifugal
Capacity:	165 gpm
Discharge Pressure:	30 ft
Size:	3 x 2 x 8
Motor HP:	5
Brake HP:	2.6
Material of Construction:	316 SS
Price:	$608

Item P3 - Zinc Sulfite Slurry Pump (1 required)

Type:	Centrifugal
Capacity:	400 gpm
Discharge Pressure:	65 ft
Size:	4 x 3 x 8
Motor HP:	7-1/2
Material of Construction:	Cast Iron
Price:	$700

Item P4 - Lean Solution Pump (1 required)

Type:	Centrifugal
Capacity:	2060 gpm
Discharge Pressure:	65 ft
Size:	10 x 8 x 11
Motor HP:	50
Brake HP:	44.1
Material of Construction:	Cast Iron
Price:	$1,076

Item P5 - Water Pump (1 required)

Type:	Centrifugal
Capacity:	765 gpm
Discharge Pressure:	60 ft
Size:	6 x 4 x 10
Motor HP:	20
Brake HP:	13.9
Material of Construction:	316 SS
Price:	$1,083

Item P6 - Gasifier Liquid Pump (1 required)

Type:	Centrifugal
Capacity:	194 gpm
Discharge Pressure:	30 ft
Size:	4 x 3 x 8
Motor HP:	15
Material of Construction:	316 SS
Price:	$838

Item P7 - Thickener Slurry Pump (1 required)

Type:	Centrifugal
Capacity:	56 gpm
Discharge Pressure:	25 ft
Size:	3 x 1-1/2 x 6
Motor HP:	3
Brake HP:	.79
Material of Construction:	316 SS
Price:	$505

Item P8 - Liming Tank Slurry Pump (1 required)

Type:	Centrifugal
Capacity:	190 gpm
Discharge Pressure:	30 ft
Size:	4 x 3 x 8
Motor HP:	5
Brake HP:	2.42
Material of Construction:	316 SS
Price:	\$838

Item V1 - Flue Gas Cyclone (1 system required)*

Capacity:	837,000 ACFM, 300°F, 732 mm (wet) Inlet Fly Ash: 87 lb/min Outlet Fly Ash: 8.7 lb/min
Pressure:	Inlet: -15 in. of water Outlet: -19 in. of water
Construction:	Welded and flanged carbon steel
Price:	\$292,500

Item V2 - Dryer Cyclone (1 system required)

Capacity:	58,300 ACFM, 250°F, 760 mm gas from dryer. Average mole weight: 35.6 (wet). Contains 0.71 lb $ZnSO_3 \cdot 2\text{-}1/2\ H_2O$ per 1000 SCF.
Pressure:	Inlet: -5 in. of water Outlet: -10 in. of water
Construction:	Welded and flanged carbon steel
Price:	\$13,000

Item V3 - Wet SO_2 Cyclone (1 system required)

Capacity:	11,570 ACFM, 600°F, 760 mm SO_2 containing 0.7 lb H_2O/lb SO_2. Contains 0.66 lb ZnO dust per 1000 SCF.
Pressure:	Inlet: +1 in. of water Outlet: -4 in. of water
Construction:	Welded and flanged carbon steel clad with type 316 SS as required.
Price:	\$7,100

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* This item or equivalent is assumed to be furnished in existing plant - Case 3.

Item V4 - Flue Gas Scrubber (quantity - see below)

Capacity:	Absorb 90 mole-% of the SO_2 from 0.55 MMSCFM of inlet flue gas containing 0.30% SO_2.
Pressure Drop:	1 in. of water with inlet pressure of 724.5 mm Hg.
Liquid Rate:	2,060 gpm of sodium sulfite·bisulfite solution at 120°F.
Type and Size:	Counter-current packed tower(s) containing a cross-sectional area of 2,187 sq ft packed with 3 in. polypropylene Intalox saddles to a depth of 8 ft. Total packing volume of approximately 17,500 cu ft. Overall height approximately 40 ft allowing for 40,000 gal reservoir, gas inlet, packing support, packing, packing hold-down, liquid distributor, mist eliminator and gas outlet.
Materials of Construction:	Fiberglass reinforced plastic and/or steel lined with protective coating.
Price:	$160,000

Although the quantity of scrubbers is not specified, it is assumed that 20% of the scrubber requirement of Cases 1 and 2 would be used.

Item V5 - Clarifier (1 required)

Capacity:	Settle and concentrate all of the ash and calcium sulfite precipitate contained 2100 gpm of feed solution into an outlet slurry. The overflow shall contain less than 2 ppm solids.
Volume:	210,000 gal
Description:	60 ft dia x 10 ft SWD resin-coated steel tank, including thickener mechanism, walkway and handrails.
Motor HP:	1-1/2
Price:	$37,835

Item V6 - Waste Thickener (1 required)

Capacity:	Settle and concentrate all of the ash and calcium sulfate precipitate contained in 193 gpm feed solution into an outlet slurry. The overflow shall contain less than 50 ppm of suspended solids.
Volume:	31,000 gal
Description:	23 ft dia x 10 ft SWD resin-coated steel tank, including thickener mechanism, walkway and handrails.
Motor HP:	1.5
Price:	$13,645

Item V7 - Zinc Oxide Tank (1 required)

Volume:	6,000 gal
Description:	11 ft dia x 8 ft SWD resin-coated steel tank with agitator.
Agitator:	10 HP
Price:	$4,400

Item V8 - Crystallizer Tank (1 required)

Volume:	30,000 gal
Description:	23 ft dia x 10 ft SWD resin-coated steel tank with agitator.
Agitator:	50 HP
Price:	$14,040

Item V9 - Gasifier Tank (1 required)

Volume:	6,000 gal
Description:	10 ft dia x 10 ft SWD fiberglass reinforced plastic closed tank.
Price:	$2,250

Item V10 - Liming Tank (1 required)

Volume: 9,000 gal

Description: 16 ft dia x 5'6" SWD fiberglass reinforced plastic tank with two compartments. Agitators in both compartments.

Agitators: 10 HP

Price: $7,675

Item V11 - Lean Solution Surge Tank (1 required)

Volume: 41,000 gal

Description: 21 ft dia x 16 ft SWD resin-coated steel tank

Price: $8,800

Item V12 - Zinc Sulfite Filter Cake Hopper (1 required)

Volume: 600 cu ft

Description: Rectangular resin-lined steel vessel with Vee bottom to a screw conveyor.

Conveyor: 5 HP

Price: $14,000

Item V13 - Dry Zinc Sulfite Hopper (1 required)

Volume: 600 cu ft

Description: Rectangular steel vessel with Vee bottom to a screw conveyor.

Conveyor: 5 HP

Price: $12,000

Item V14 - Zinc Sulfite Thickener (1 required)

Capacity: Settle and concentrate all of the zinc sulfite precipitate contained in 1730 gpm of feed solution into an outlet slurry. The overflow shall contain less than 2 ppm solids.

Volume: 210,000 gal

Description: 60 ft dia x 10 ft SWD resin-coated steel tank, including thickener mechanism, walkway and handrails.

Motor HP: 1-1/2

Price: $37,835

APPENDIX C-4

ZINC OXIDE PROCESS

Case 4

Equipment List

Item C1 - Smelter Gas Blower (1 required)

Capacity:	310,000 ACFM
Static Pressure:	8 in. S.W.G.
Motor HP:	700
Brake HP:	655
Price:	$50,000

Item C2 - Dryer Gas Blower (1 required)

Capacity:	266,000 ACFM
Static Pressure:	5 in. S.W.G.
Motor HP:	300
Brake HP:	280
Price:	$38,000

Item C3 - SO_2 Recycle Compressor (1 required)

Capacity:	1610 ACFM
Intake Pressure:	14.7 psia
Discharge Pressure:	22.7 psia
Intake Temperature:	120°F
Discharge Temperature:	203°F
Motor HP:	100
Price:	$6,863

Item E1 - SO_2-H_2OCondenser (1 required)

Type:	Direct contact packed column
Size:	11 ft dia. x 20 ft high steel column, epoxy resin coated
Packing:	770 cu ft 3 in. stoneware, Intalox saddles
ΔP:	2.4 in. S.W.G. across packing
Price:	$16,000

Item E2 - Heat Exchanger (1 required)

Duty:	77,000,000 Btu/hr
Area:	1450 sq ft
Size:	34 in. I. D. steel shell
Tubes:	3/4 in. O. D. x 20 ft long, type 316 SS
Tube Plates:	C. S. clad with type 316 SS
Price:	$46,000

Item M1 - Waste Filter (1 required)

Type:	Vacuum Drum Filter, 12 ft dia x 18 ft long, 670 sq ft rubber-covered; complete with filtrate receiver, moisture trap, filtrate pump and vacuum pump.
Capacity:	200 tons/day dry cake
Total Motor HP:	85
Price:	$80,000

Item M2 - Zinc Sulfite Centrifuge (4 required)

Type:	36 in. x 96 in. screen bowl centrifuge
Motor HP:	250
Capacity:	26 ton/hr solids
Price:	$65,000

Item M3 - Zinc Sulfite Dryer (1 required)

Type:	Rotary dryer, concurrent flow, indirect heating
Capacity:	3350 lb/min zinc sulfite with 20% free water dried to a product containing not more than 2% free water
Size:	10 ft diameter x 100 ft long
Motor HP:	200
Price:	$142,000

Item M4 - Hammer Mill (3 required)

Type:	18 in. direct-coupled, 1800 RPM
Motor HP:	50
Capacity:	43 ton/hr, - 100 mesh
Price:	$3,110

Item M5 - Flash Calciner (1 required)

Type:	Vertical furnace with stainless steel radiant tubes for continuous operation of 1400°F wall temperature.
Heat Duty:	151 million Btu/hr
Capacity:	110 tons per hour of zinc sulfite · 2-1/2 H_2O with 2% free water, heating it to 600°F minimum thereby flashing off water and sulfur dioxide.
Feed Temperature:	200°F
Price:	$402,000

Item M6 - Zinc Sulfite Conveyor (2 required)

Type:	Screw conveyor, enclosed
Size:	20 in. dia x 100 ft long
Capacity:	2250 lb/min wet cake
Material of Construction:	Coated steel
Motor HP:	25
Price:	$9,300

Item M7 - Zinc Sulfite Conveyor (1 each required)

a.	Type:	Screw conveyor, enclosed
	Size:	20 in. dia x 120 ft long
	Capacity:	3700 lb/min dry material
	Motor HP:	25
	Price:	$11,000
b.	Type:	16 x 8 bucket, 60 ft vertical
	Capacity:	3700 lb/min dry material
	Motor HP:	20
	Price:	$5,300

Item M8 - Zinc Oxide Conveyor (1 each required)

a.	Type:	Screw conveyor, enclosed
	Size:	20 in. dia x 45 ft long
	Capacity:	1570 lb/min
	Motor HP:	5
	Price:	$4,700
b.	Type:	16 x 8 bucket, 30 ft vertical
	Capacity:	1570 lb/min
	Motor HP:	10
	Price:	$3,800

Item M9 - Lime Hopper/Feeder (1 required)

Surge Capacity:	50 cu ft
Feed Capacity:	100 lb/min
Motor HP:	[illegible]
Price:	$6,000

Item M10 - Soda Ash Hopper/Feeder (1 required)

Surge Capacity:	50 cu ft
Feed Capacity:	10 lb/min
Motor HP:	1
Price:	$6,000

Item M11 - Zinc Oxide Hopper/Feeder (1 required)

Surge Capacity:	50 cu ft
Feed Capacity:	5 lb/min
Motor HP:	1
Price:	$6,000

Item M12 - Zinc Sulfite Hopper/Feeder (1 required)

Surge Capacity:	500 cu ft
Feed Capacity:	3700 lb/min
Motor HP:	10
Price:	$13,000

Item M13 - Waste Conveyor (1 required)

Type:	12 in. inclined belt, 150 ft long
Capacity:	440 lb/min
Motor HP:	15
Price:	$6,400

Item M14 - Furnace (1 required)

Type:	Gas or oil-fired standard combustion chamber
Heat Duty:	45 million Btu/hr
Price:	$45,000

Item P1 - Rich Solution Pump (2 required)

Type:	Centrifugal
Capacity:	4650 gpm
Discharge Pressure:	24 ft
Size:	14 x 14 x 20
Motor HP:	40
Brake HP:	40
Material of Construction:	316 SS
Price:	$5,800

Item P2 - Clarifier Slurry Pump (1 required)

Type:	Centrifugal
Capacity:	830 gpm
Discharge Pressure:	30 ft
Size:	6 x 4 x 13
Motor HP:	10
Material of Construction:	316 SS
Price:	$1,727

Item P3 - Zinc Sulfite Slurry Pump (1 required)

Type:	Centrifugal
Capacity:	1840 gpm
Discharge Pressure:	65 ft
Size:	10 x 8 x 11
Motor HP:	40
Brake HP:	39.3
Material of Construction:	Cast Iron
Price:	$1,030

Item P4 - Lean Solution Pump (2 required)

Type:	Centrifugal
Capacity:	4650 gpm
Discharge Pressure:	65 ft
Size:	14 x 14 x 20
Motor HP:	125
Brake HP:	105
Material of Construction:	Cast Iron
Price:	$3,800

Item P5 - Water Pump (2 required)

Type	Centrifugal
Capacity:	1700 gpm
Discharge Pressure:	60 ft
Size:	10 x 8 x 11
Motor HP:	40
Brake HP:	30.8
Material of Construction:	316 SS
Price:	$2,480

Item P6 - Gasifier Liquid Pump (1 required)

Type:	Centrifugal
Capacity:	860 gpm
Discharge Pressure:	30 ft
Size:	6 x 4 x 3
Motor HP:	15
Material of Construction:	316 SS
Price:	$1,787

Item P7 - Thickener Slurry Pump (1 required)

Type:	Centrifugal
Capacity:	243 gpm
Discharge Pressure:	25 ft
Size:	4 x 3 x 8
Motor HP:	5
Brake HP:	2.3
Material of Construction:	316 SS
Price:	$838

Item P8 - Liming Tank Slurry Pump (1 required)

Type:	Centrifugal
Capacity:	840 gpm
Discharge Pressure:	30 ft
Size:	6 x 4 x 13
Motor HP:	10
Material of Construction:	316 SS
Price:	$1,727

Item P9 - Prescrubber Circulating Pump (3 required)

Type:	Centrifugal
Capacity:	5600 gpm
Discharge Pressure:	65 ft
Size:	16 x 18 x 18
Motor HP:	300
Brake HP:	239
Material of Construction:	Carp. 20
Price:	$16,000

Item VI - Smelter Gas Prescrubber

a. Gas - 210,000 SCFM at 760 mm Hg & 32°F

	Inlet Gas			Outlet Gas		
	mole %	moles/min	lb/min	mole %	moles/min	lb/min
SO_2	2.9	17.0	1090	2.6	17.0	1090
CO_2	1.7	9.9	437	1.5	9.9	437
CO	0.6	3.5	98	0.5	3.5	98
H_2O	0.1	0.6	10	10.9	71.6	1289
O_2	14.3	83.7	2677	12.8	83.7	2677
N_2	80.4	470.3	13169	71.7	470.3	13169
H_2SO_4		-	1.25		-	0.0
Dust		-	6.0		-	0.3
		585.0	17488		656.0	18760

Temperature, °F	440	117
Pressure, inches W.C.	0	-6

b. Liquid

	Inlet	Outlet
GPM	15,300	15,145

Type and Size: Flooded bed, turbulent layer, 3 stage, with a cross-sectional area of approximately 420 sq ft. Over-all height approximately 40 ft allowing for gas inlet, three mobile stages, liquid distributor, mist eliminator and gas outlet.

Materials of Construction: Steel lined with corrosion resistant protective coating.

Price: \$175,000

Note: It is assumed that this type scrubber will absorb all of the H_2SO_4 and remove 95% of the dust. If 99%+ dust removal is needed, a high energy type prescrubber, such as the wet venturi or flooded disk, may be needed. The high energy type unit would probably require a high power input, i.e. a Δp of 50-80 inches of water, to achieve the high particulate removal efficiency.

Item V2 - Dryer Cyclone (1 system required)

Capacity: 249,000 ACFM, 250°F, 760 mm gas from dryer. Average mole weight: 35.6 (wet). Contains 0.71 lb $ZnSO_3 \cdot 2\ 1/2\ H_2O$ per 1000 SCF.

Pressure: Inlet: -5 in. of water
Outlet: -10 in. of water

Construction: Welded and flanged carbon steel

Price: \$70,000

Item V3 - Wet SO_2 Cyclone (1 system required)

Capacity: 52,000 ACFM, 600°F, 760 mm SO_2 containing 0.7 lb H_2O/lb SO_2. Contains 0.66 lb ZnO dust per 1000 SCF

Pressure: Inlet: +1 in. of water
Outlet: -4 in. of water

Construction: Welded and flanged carbon steel clad with type 316 SS as required

Price: \$43,000

Item V4 - Flue Gas Scrubber (quantity - see below)

Capacity:	Absorb 95 mole % of the SO_2 from 210,000 SCFM of inlet smelter gas containing 2.9% SO_2.
Pressure Drop:	2 in. of water with inlet pressure of -6 in. of water.
Liquid Rate:	9300 gpm of sodium sulfite-bisulfite solution at 120°F.
Type and Size:	Counter-current packed tower(s) containing a cross-sectional area of 1200 sq ft packed with 3 in. polypropylene Intalox saddles to a depth of 13 ft. Total packing volume of approximately 15,600 cu ft. Over-all height approximately 45 ft allowing for 40,000 gal reservoir, gas inlet, packing support, packing, packing hold-down, liquid distributor mist eliminator, and gas outlet.
Materials of Construction:	Fiberglas reinforced plastic and/or steel-lined with protective coating.
Price:	$200,000

Although the quantity of scrubbers is not specified, the total cross-sectional area will equal 1200 sq ft.

Item V5 - Clarifier (1 required)

Capacity:	Settle and concentrate all of the calcium sulfite precipitate (and dust, if any) contained in 9,300 gpm of feed solution into an outlet slurry. The overflow shall contain less than 2 ppm solids.
Volume:	970,000 gal
Description:	134 ft dia x 10 ft SWD resin-coated steel tank including thickener mechanism walkway and handrails.
Motor HP:	10
Price:	$93,000

Item V6 - Waste Thickener (1 required)

Capacity:	Settle and concentrate all of the calcium sulfate precipitate (and dust, if any) contained in 860 gpm feed solution into an outlet slurry. The overflow shall contain less than 50 ppm of suspended solids.
Volume:	120,000 gal
Description:	45 ft dia x 10 ft SWD resin-coated steel tank, including thickener mechanism, walkway and handrails.
Motor HP:	2
Price:	$23,500

Item V7 - Zinc Oxide Tank (1 required)

Volume:	28,000 gal
Description:	22 ft dia x 10 ft SWD resin-coated steel tank with agitator.
Agitator:	60 HP
Price:	$16,000

Item V8 - Crystallizer Tank (1 required)

Volume:	138,000 gal
Description:	48 ft dia x 10 ft SWD resin-coated steel tank with agitator
Agitator:	250 HP
Price:	$47,000

Item V9 - Gasifier Tank (1 required)

Volume:	30,000 gal
Description:	23 ft dia x 10 ft SWD resin-coated steel tank
Price:	$8,300

Item V10 - Liming Tank (1 required)

Volume:	47,000 gal
Description:	32 ft dia x 8 ft SWD resin-coated steel tank with two compartments. Agitators in both compartments.
Agitator:	40 HP
Price:	$19,000

Item V11 - Lean Solution Surge Tank (1 required)

Volume:	180,000 gal
Description:	56 ft dia x 10 ft SWD resin-coated steel tank
Price:	$22,500

Item V12 - Zinc Sulfite Filter Cake Hopper (1 required)

Volume:	2500 cu ft
Description:	Rectangular resin-lined steel vessel with Vee bottom to a screw conveyor.
Conveyor:	25 HP
Price:	$29,000

Item V13 - Dry Zinc Sulfite Hopper (1 required)

Volume:	2300 cu ft
Description:	Rectangular steel vessel with Vee bottom to a screw conveyor.
Conveyor:	25 HP
Price:	$26,000

Item V14 - Zinc Sulfite Thickener (1 required)

Capacity:	Settle and concentrate all of the zinc sulfite precipitate contained in 9100 gpm of feed solution into an outlet slurry. The overflow shall contain less than 2 ppm solids.
Volume:	970,000 gal
Description:	134 ft dia x 10 ft SWD resin-coated steel tank, including thickener mechanism, walkway and handrails.
Motor HP:	10
Price:	$93,000

Item V15 - Prescrubber Surge Tank

Volume:	130,000 gal
Description:	48 ft dia x 10 ft SWD resin-coated steel tank.
Price:	$18,500

APPENDIX C-5

LIME PROCESS

Case 3

Equipment List

Item 1 - Flue Gas Scrubber (3 required)

Capacity:	Absorb 90 mole-% of the SO_2 from 180,000 SCFM of inlet flue gas containing 0.30% SO_2
Pressure Drop:	10 in. maximum of water with inlet pressure of 15 in. S.W.G.
Liquid Rate:	13,300 gpm of 10% slurry at 120°F.
Type and Size:	Flooded bed, turbulent layer, 3 stage, with a cross-sectional area of approximately 300 sq ft. Over-all height approximately 40 ft allowing for gas inlet, three mobile stages, liquid distributor, mist eliminator and gas outlet.
Materials of Construction:	Steel lined with corrosion-resistant protective coating.
Price:	$100,000

Item 2 - Flue Gas Blower (2 required)

Capacity:	335,500 ACFM @ 548 RPM
Static Pressure:	10 in. S.W.G.
Motor HP:	600
Brake HP:	564
Wheel Diameter:	7 ft 5 in.
Price:	$45,000

Item 3 - Slurry Surge Tank (1 required)

Volume:	30,000 gal
Description:	23 ft dia x 10 ft deep resin-coated steel tank with agitator.
Agitator:	50 HP
Price:	$14,000

Item 4 - Limestone Hopper/Feeder (1 required)

Hopper Capacity:	500 ft^3
Feed Capacity:	500 lb/min
Motor HP:	5
Price:	$13,000

Item 5 - Slurry Mixing Tank (1 required)

Volume:	50,000 gal
Description:	33 ft dia x 8 ft deep resin-coated steel tank with two compartments. Agitators in both compartments
Agitator:	40 HP
Price:	$19,700

Item 6 - Slurry Disposal Pump - P1, (1 required)

Type:	Centrifugal
Capacity:	1000 gpm
Discharge Pressure:	24 ft
Size:	6 x 4 x 13
Motor HP:	15
Material of Construction:	Cast Iron
Price:	$900

Item 7 - Slurry Recirculating Pump - P2, (3 required)

Type:	Centrifugal
Capacity:	14,000 gpm
Discharge Pressure:	65 ft
Size:	18 x 16 x 18
Motor HP:	350
Material of Construction:	Cast Iron
Price:	$9400

Item 8 - Recycle Water Pump - P3, (1 required)

Type:	Centrifugal
Capacity:	750 gpm
Discharge Pressure:	65 ft
Size:	6 x 4 x 13
Motor HP:	20
Material of Construction:	Cast Iron
Price:	$1000

Item 9 - Slurry Make-Up Pump - P4, (1 required)

Type:	Centrifugal
Capacity:	750 gpm
Discharge Pressure:	65 ft
Size:	6 x 4 x 13
Motor HP:	20
Material of Construction:	Cast Iron
Price:	$1000

END